

# Solution Properties of Sidechain Polymers For Enhanced Oil Recovery

by

Yahya Garba Oloriegbe

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**CHEMICAL ENGINEERING**

January, 1994

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**Oloriegbe, Yahya Garba, M.S.**

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Dhahran 31261, Saudi Arabia

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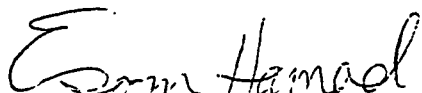
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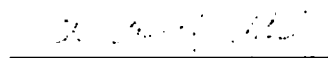
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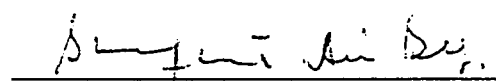
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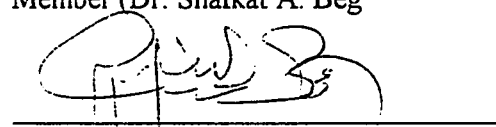
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## **DEDICATION**

**This Thesis is Dedicated to My Parents.**



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## LIST OF SYMBOLS AND NOTATIONS

$N_c$	Capillary Number
$\mu_w$	Viscosity of Water or Displacing Fluid
$q$	Flowrate per unit cross-sectional area of water
$\gamma_{o/w}$	Interfacial tension Between Oil and Water
$\phi$	Porosity of the Petroleum Reservoir
$\Delta P$	Pressure Drop Across the Interface of Water and Oil
$r$	The radius of the porous media
$M$	Water-Oil Mobility Ratio
$K_w$	Effective Water or Displacing Fluid Permeability of the Reservoir Rock, in the Zone Occupied by the Fluid.
$K_o$	Oil Permeability of the Reservoir Rock, in the Zone Occupied by the Oil.
$\mu_o$	Viscosity of Oil
$A_{co}$	Solvent Attraction Between Surfactant and Oil.
$A_{cw}$	Solvent Attraction Between Surfactant and Water.

RPM	Revolution per minute
$\sigma$	Surface or Interfacial tension (mN/m)
L	Wetted Length of Ring or Plate
F	Measured Force
$K_{\max}$	Maximum Force (nM)
$l_b$	Wetted length (m)
$F_{cr}$	The Correction factor which accounts for the weight of the liquid lifted, while the Ring is removed
K	Measured Force (nM)
$\theta$	Angle of Wetting
APS	Ammonium per Sulfate
DMSO	Dimethyl sulfoxide
T-BUP	Tertiary butylhydroperoxide
a,b,c,n & m	Repeat Units
X	Chloride or Bromide ion
DMF	Dimethyl formamide
C22	Docosanoic acid alkyl chain

<b>C18</b>	<b>Stearic acid alkyl chain</b>
<b>C10</b>	<b>Decanoic acid alkyl chain</b>
<b>IFT</b>	<b>Interfacial tension</b>
<b>PVA</b>	<b>Polyvinyl alcohol</b>

## THESIS ABSTRACT

**NAME OF STUDENT** : Yahya Garba Oloriegbe  
**TITLE OF STUDY** : *Solution Properties of Sidechain Polymers for Enhanced Oil Recovery*  
**MAJOR FIELD** : *Chemical Engineering*  
**DATE OF DEGREE** : *January, 1994*

*In this study, three classes of amphiphilic sidechain polymers are synthesized or modified, with the objective of investigating their rheological behaviour and surface and interfacial activities for enhanced oil recovery applications. The polymers considered are, cyclopolymer of diallyl quaternary ammonium salt, copolymers of maleic anhydride/1-alkene and hydrophobically modified polyvinylalcohol (PVA). The rheological behaviour and surface and interfacial activities of these polymers are studied with respect to the polymers concentration, temperature, salinity, shear rate, polymers molecular weight and time.*

*The viscosity of the diallyl quaternary ammonium chloride cyclopolymer and the maleic anhydride/1-alkene copolymers is characteristically low, up to high polymer concentrations. However, the solution viscosity of the hydrophobically modified PVA is found relatively high at moderate polymer concentrations. Furthermore, the aqueous solution of the cyclopolymer and the copolymers exhibit low salt tolerance, typical of polyelectrolyte polymers, in the range of 0-1.0wt% NaCl concentrations. On the other hand, the hydrophobically modified PVA exhibits a relatively high salt tolerance, typical of nonionic polymers, in the range of 0-7.0 wt% NaCl concentrations. Moreover, good surface and interfacial activities, including low surface and interfacial tensions are exhibited by all the three classes of polymers considered in this work. It is also found that adding NaCl to the copolymers and the hydrophobically modified PVA in aqueous solution increases their surface and interfacial activities. The viscosity of the hydrophobically modified PVA and the copolymers have been found to be relatively invariant with NaCl above 3.0 wt% and 0.1 wt% NaCl concentrations respectively. The hydrophobically modified PVA with high molecular weight exhibits a greater thickening ability and higher surface and interfacial activities than the one with low molecular weight. A slight decrease in viscosity is also exhibited by the modified polymer with time.*

*Generally, the three classes of polymers considered in this work exhibit an almost constant viscosity at high shear rates and a typical shear thinning behaviour at low shear rates. In addition, increasing polymer concentration leads to an increase in the polymer solution viscosity and decrease in surface and interfacial tensions. Moreover, the polymers exhibit smaller solution viscosity at high temperature.*

*From this study, it seems possible to design polymers that can simultaneously provide high viscosity and ultra-low interfacial tension for use in enhanced oil recovery operations.*

**MASTER OF SCIENCE DEGREE**

**KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS**

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## خلاصة الرسالة

- اسم الطالب الكامل : يحيى جاربا أولوريجي .  
عنوان الرسالة : خصائص محاليل البوليمرات ذات السلاسل الجانبية لاستخدامها في استخراج البترول بالطريقة المعززة .  
التخصص : الهندسة الكيميائية .  
تاريخ الشهادة : يناير ١٩٩٤ م .

في هذا البحث تم تصنيع أو تعديل ثلاثة أصناف من البوليمرات ثنائية الخواص ذات السلاسل الجانبية بهدف دراسة سلوكها اللزجي ونشاطها السطحي والبين سطحي لاستخدامها في عمليات استخراج البترول بالطريقة المعززة . البوليمرات التي أخذت في الاعتبار تشمل بوليمر حلقي ملح رباعي (Quaternary) لداي البيل أمونيوم Diallyl quaternary ammonium salt وأيضاً بوليمرات تناوبية للملك انهايديراد/١- الكيني Maleic anhydride/1-alkene وبولي فاينيل الكحول المعدل هايدروفوبيكياً (PVA) Hydrophobically modified polyvinylalcohol . لقد تم دراسة السلوك اللزجي والنشاط السطحي والبين سطحي لهذه البوليمرات مع تغير تركيز البوليمر ودرجة الحرارة والملوحة ومعدل الشد والوزن الجزيئي لهذه البوليمرات وأيضاً الزمن .

لقد وجد أن لزوجة البوليمر الحلقي والبوليمر التناوبي تكون منخفضة بشكل مميز إلى حد تراكيز بوليمرية عالية . إلا أن لزوجة محلول البولي فاينيل الكحول المعدل كانت عالية عند تركيز معتدل للبوليمر . علاوة على ذلك وجد أن المحلول المائي للبوليمر الحلقي والبوليمرات التناوبية يتأثر كثيراً بالتركيز الملحي ، وذلك متوقع للبوليمرات الإلكتروليتية Polyelectrolytes ، في مدى ٠.٠٠ - ١٪ وزن لتركيز ملح الطعام . ولكن وجد أن بولي فاينيل الكحول المعدل يتحمل تركيز ملحي عالي نسبياً ، وذلك متوقع للبوليمرات الغير أيونية ، في مدى ٠ - ٧٠٪ وزن لتركيز ملح الطعام . بالإضافة إلى ذلك ، كل أصناف البوليمرات الثلاثة التي أخذت في الاعتبار قد وُجد أن لها نشاط سطحي وبن سطحي جيد ( شد سطحي وبن سطحي منخفض ) . ولقد وجد أيضاً أن إضافة NaCl إلى كل من المحاليل المائية للبوليمرات التناوبية والبولي فاينيل الكحول المعدل ، يزيد من نشاطها السطحي والبن سطحي . ولوحظ أن لزوجة هذه المواد نسبياً غير متغيرة مع NaCl بتركيز أقل من ١٠٪ وزن للبوليمرات التناوبية و ٣٪ وزن للبولي فاينيل الكحول المعدل . وهذا الأخير المحتوي على وزن جزيئي عالي لوحظ أنه قد أعطى قدرة عالية للتشنج ونشاط سطحي وبن سطحي عال عن نفس البوليمرات بوزن جزيء منخفض . لقد لوحظ أيضاً أن هناك انخفاض بسيط في لزوجة البوليمر المعدل مع الزمن .

عامة ، الثلاثة أصناف من البوليمرات التي درست في هذا البحث وجد أن علاقة ( اللزوجة - معادل الشد ) لها تسلك غالباً لزوجة ثابتة عند معدلات شد عالية وتسلك أيضاً شد ترقبتي نموذجي عند معدلات شد منخفضة . بالإضافة إلى ذلك زيادة تركيز البوليمر يقود إلى زيادة في لزوجة محلول البوليمر وانخفاض في الشد السطحي والبن سطحي . علاوة على ذلك ، البوليمرات المدروسة وجد أنها تسلك انخفاض في محلول اللزوجة مع الزيادة في درجة الحرارة .

من هذه الدراسة ، تبين أنه من الممكن تصميم بوليمرات باستطاعتها أن توفر لزوجة عالية وبنفس الوقت شد بين سطحي منخفض جداً وذلك لأجل استخدام هذه البوليمرات في عمليات استخراج البترول بطريقة التعزيز .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

يناير ١٩٩٤ م



## CHAPTER 1

### INTRODUCTION

In oil production technology, there are three basic stages of oil recovery techniques. They include primary, secondary and tertiary or enhanced oil recovery. Forty to sixty percent of the original oil in place typically remains trapped in the reservoir after primary and secondary recoveries. Methods which attempt to recover this trapped oil, termed enhanced oil recovery (EOR), are classified into thermal, miscible and chemical flooding. Thermal flooding involves injection of steam or in-situ combustion into the petroleum reservoir to reduce the viscosity of the oil in order to facilitate the oil movement to the production wells. Miscible flooding involves injection of a fluid such as carbon dioxide into the petroleum reservoir to mix with the oil so as to reduce the capillary forces or lower the interfacial tension between the oil and drive water. Thus enhances the microscopic displacement efficiency of the drive water. Chemical flooding involves injection of chemical additives, such as polymers and surfactants that can modify the properties of drive water in the petroleum reservoir in favour of oil production. The goal of chemical flooding is to increase the sweep efficiency and microscopic displacement efficiency of the drive water.

Current chemical methods in which a lot of work has been done include the conventional polymers and surfactant-polymer floodings. The methods involve injection of aqueous solutions of surfactant and water soluble polymers into the petroleum reservoir. The polymer solution provides mobility control and also increases the sweep efficiency, while the surfactant solutions are designed to

yield low interfacial tension in the reservoir. The polymers currently being used in this method rely on a combination of high molecular weight and chain expansion. However, high molecular weight polymers are sensitive to high shear stress. This can cause permanent degradation of the polymer. Also the presence of ions, especially divalent, in the solution shields the ionic groups on the polymer, causing it to collapse in to a random coil. Thus reducing the polymer thickening ability. Another problem with the current surfactant-polymer flooding is the surfactant-polymer incompatibility. Adsorption of surfactant molecules on the reservoir rocks also causes a major problem, because of the loss of these relatively expensive chemicals [2,3].

The problems with the current chemical methods can be avoided by using polymers that can associate in aqueous solutions [1]. Association in aqueous solutions can be promoted by incorporating hydrophobic moieties (sidechains) into the polymer structure. Association causes the formation of aggregates with large hydrodynamic radii, which are the key to the thickening ability. The advantage of associative sidechain polymers over the current polymers methods is that the association process is reversible. Which implies that, during high shear rate or other unfavourable conditions, when the aggregates are separated into individual molecules, the aggregates can reform once the cause is gone and the solution can regain its high viscosity [1]. This mechanism could alleviate the permanent polymer degradation due to molecular scission, and could also reduce the effect of high ionic concentration on the hydrodynamic radii of the aggregates. In addition, the adsorption of polymer molecules on rock surfaces, is expected to be smaller than the adsorption of surfactant molecules at the same conditions, because of the unfavorable configuration changes that the large

polymer molecules suffer during adsorption [1]. This view is supported by Chou et.al [5], who reported low adsorption for an oligomeric surfactant (surfactant with a short polymer chains). Another advantage of hydrophobic polymers is their compatibility with surfactants as a result of presence of hydrophobic groups in both [1]. However, this concept may fail in surfactant-polymer systems, because McCormick et.al [1,4], found that the presence of surfactant molecules can reduce the extension of association among the polymer molecules due to competition for association by the surfactant molecules with the polymer molecules. Reduced association among polymer molecules can result in a reduction in viscosity. It has been recognized that a property of most hydrophobic polymers, which has not been discussed from the enhanced oil recovery point of view so far, at least to our knowledge is their ability to reduce or lower the interfacial tension. The reason for this ability is the amphiphilic nature of these polymers, a property they share with surfactants. Thus the problem of competition for association between surfactant and polymer molecules could be avoided. Since the low interfacial tension required from surfactant can now be obtained from the hydrophobic polymer. From the hydrophobic polymer, high viscosity and low interfacial can be achieved at the same time. Thus it may not be necessary any longer to use surfactant in enhanced oil recovery operations. High viscosity can be obtained from hydrophobic polymer as a result of hydrophobic association being promoted by the hydrophobic groups attached. Hence from the associative sidechain polymers, the sought properties are low oil-water interfacial tension (IFT) and high viscosity. The low oil-water interfacial tension is necessary, because capillary forces, which depend on the IFT, limit the microscopic displacement

efficiency of water. Furthermore, the pressure drop across the interface of oil-water is directly proportional to interfacial tension (IFT) and inversely proportional to pore radius. As such decrease in IFT will ultimately causes reduction in pressure drop, which reduces the energy consumption of the enhanced oil recovery operations. This reduction will also leads to a decrease in the limitation of the microscopic displacement efficiency of drive water caused by the capillary forces. High viscosity is necessary for efficient oil sweep, because for a stable displacement each fluid bank should be less mobile than the one it is displacing. It is therefore the aim and objective of this research **to design and test sidechain graft associative polymers that can simultaneously provide aqueous solutions with both mobility control and low interfacial tension.** A polymer possessing these two properties can overcome many problems in enhanced oil recovery.

In order to achieve these objectives, three classes of polymer synthesis and modification have been considered in this research. They include copolymerization of 1-alkene with maleic anhydride, hydrophobically modification of urethanized polyvinyl alcohol (PVA) and cyclopolymerization of diallylamine derivatives. The solution properties of these polymers, such as viscosity behaviour and surface and interfacial activities have been determined by using a Brookfield digital viscometer and Plate and Ring methods Tensiometer.

Enhanced oil recovery technique is not exclusively an area of petroleum engineers. Chemical engineers also have roles to play in this area. Basic knowledge of chemical engineering principles such as fluid flow in porous media,

heat transfer, phase behaviour, interfacial phenomena and multicomponent adsorption are essential in maximizing oil recovery from existing oil fields and also to develop many of the existing enhanced oil recovery techniques.

The efficient recovery of oil reserves is of great importance for Saudi Arabia as well as for the rest of the world. Therefore improving enhanced oil recovery methods and developing detailed knowledge about the fabrication of polymers are important for the future oil production and self-sufficiency of the kingdom. Especially that the left-behind oil, after primary and secondary recovery stages is about two-third or more of the original oil in place; oil also remains a major and difficult-to-replace source of energy, especially for transportation, and of raw-materials for the petrochemical industries. Indeed, enhanced oil recovery is an ongoing technology open to great improvements.

The present study has been initiated with the following objectives :

- a) To modify and synthesize hydrophobically associating water-soluble polymers.
- b) To study the rheological behaviour of the polymers in aqueous solution, with respect to the polymers concentration, temperature, salinity, different values of shear rate and polymers molecular weight.
- c) To measure the surface and oil-water interfacial tensions of the polymers with respect to the polymers concentration, temperature, salinity and polymers molecular weight.

- d) To study the stability of the polymers solution properties by measuring viscosity over a long period of time (ageing).

## CHAPTER 2

### LITERATURE REVIEW

Enhanced oil recovery (EOR) generally refers to the additional recovery of oil from a petroleum reservoir over and above that which can be economically recovered by conventional primary and secondary methods [13]. Within this broad definition there are a variety of processes. These include various forms of waterflooding, caustic flooding, hydrocarbon injection, carbon dioxide flooding, micellar-polymer flooding, surfactant-polymer flooding and several thermal methods [6]. Enhanced oil recovery consists of methods aimed at increasing ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents, oxidizers and heat carriers, in order to induce new mechanisms for displacing oil. Oil remaining trapped after primary and secondary recovery is the target of the enhanced oil recovery [13]. At the end of secondary recovery (i.e. water flooding), the residual oil is believed to be in form of immobile globules distributed through the pores of the rock in the petroleum reservoir. The two major forces acting on these immobile globules are capillary forces and viscous forces. The ratio of viscous to capillary forces with the oil recovery efficiency in porous media has been correlated with the capillary number,  $N_c$ , [7], where

$$N_c = \mu_w \phi \frac{q}{\gamma_{o/w}} \quad (2.1)$$

It is generally recognized that as the capillary number increases, the oil displacement efficiency also increases [7]. The increase in capillary number can

be achieved by either increasing the viscosity of drive water,  $\mu_w$ , or decreasing the interfacial tension between oil and drive water,  $\gamma_{o/w}$ , or both. It is also generally believed that the lower the pressure drop,  $\Delta P$ , across the interface of water and oil, the higher the oil displacement efficiency as can be seen in equation 2.2 [7], where

$$\Delta P = 2 \frac{\gamma_{o/w}}{r} \quad (2.2)$$

This can be achieved by lowering the interfacial tension between the oil and the drive water,  $\gamma_{o/w}$ . An ultra-low interfacial tension between the oil and the brine should be required for easy flow of trapped oil drops, because it reduces the work of deformation needed for oil ganglia to move through the narrow necks of pore channels. The sweep efficiency of water flooding can be improved by lowering the water-oil mobility ratio,  $M$ , expressed as [54],

$$M = k_w \frac{\mu_o}{k_o \mu_w} \quad (2.3)$$

Also the proportion of the unswept area depends greatly on mobility ratio, which can be decreased by either lowering the viscosity of the oil,  $\mu_o$ , or increasing the viscosity of the displacing fluid, (i.e water),  $\mu_w$ , as can be seen from eq 2.3.

In view of all these, it is necessary to have an ultralow interfacial tension between the oil and the drive water, and a high viscosity of the displacing fluid for efficient enhanced oil recovery operations. Chemical flooding methods are considered in this work, because of their wide applicability.



## 2.1 SURFACTANT - POLYMER FLOODING STUDIES

Surfactant-polymer flooding is one of the most important current tertiary recovery methods. A lot of work has been done to investigate this method [2,8–15]. The conventional water-soluble polymers and surfactant-polymer flooding have gained a great deal of interest in the petroleum industry over the years. In enhanced oil recovery techniques, these polymers are used for mobility control to improve the performance of water flooding operations. Such polymers are mainly used as viscosifying agents for the water injected to control the water front advancement inside the reservoir, while the surfactant solutions are used to lower the interfacial tension. Surfactant-polymer flooding involves successive injection into the reservoir of an aqueous or surfactant slug and a dilute polymer solution. During this process, the displaced oil droplets coalesce and form an oil bank. Once an oil bank is formed in the porous medium, it has to be propagated through the porous medium with minimum entrapment of oil at the trailing edge of the oil bank. The maintenance of ultralow interfacial tension at the oil bank/surfactant interface is necessary for minimising the entrapment of the oil in the porous medium. The leading edge of the oil bank coalesces with additional oil ganglia [3].

Among the investigators of this method, Totonji et. al [10], studied the application of surfactant-polymer flooding under the particular conditions of Saudi Arabia oil reservoirs and found that the surfactant-polymer method used should recover up to 30 percent of the residual oil under the salinity conditions and temperature of Saudi Arabia reservoirs. Shah et.al [14], also reviewed a lot of work on surfactant-polymer flooding method. Typical studies are on oil

recovery with surfactants, flow of polymers through porous media in relation to oil displacement and mechanisms of polymer retention in porous media. Baviere et.al [13], also reviewed some work on this method. Some of which are the studies of mobility control by polymers and reduction of capillary forces by surfactants. Donaldson et.al [15], also reviewed this method and actually studied polymer flooding and the use of surfactants in oil recovery

## 2.2 ASSOCIATIVE SIDECCHAIN POLYMERS STUDIES

The application of amphiphilic polymers to replace the current chemical method (i.e surfactant-polymer flooding) in providing low interfacial tension and at the same time mobility control is a novel ideal. The use of partially hydrophobilized polymers to improve the viscosification efficiency of brine solutions is one of the current concepts in the literature. Many workers in enhanced oil recovery methods have reported solution viscosity of the polymers. [16–27], but no one has actually reported hydrophobilized polymers solution interfacial tension behaviour, atleast to our knowledge. It is an objective of this research to relate the interfacial tension to the structure of the polymer. Such relationship can then be used to design polymers which are capable of reducing the interfacial tension of oil-water interface to a very low values (in the order of  $10^{-3}$  mN/m). It might then be possible to use such polymers to simultaneously achieve ultralow interfacial tension and mobility control. If an inexpensive polymer can be developed to provide the two features or properties,

then the design of chemical enhanced oil recovery could be simplified and the problems with the conventional surfactant-polymer and polymer flooding can be avoided [1].

Bock et.al [16], investigated the use of hydrophobically associating polymers containing N-vinyl-pyrrolidone functionality for enhanced oil recovery. These polymers, when dissolved in an aqueous brine solution have the ability to substantially increase the viscosity of the aqueous solution. The control of displacement fluid mobility results in more uniform sweep efficiency and improved oil recovery. In addition, aqueous solutions of these hydrophobically associating polymers exhibit enhanced viscosification, reduced salt sensitivity and other desirable rheological properties found useful in chemically enhanced oil recovery processes. Wang et.al [17], studied the viscometric behaviour of hydrophobically modified poly(sodium acrylate) and found the modified polymer aqueous solution to exhibit a very high thickening power. Schulz et.al [18], reported the synthesis and solution properties of the copolymer of acrylamide and surfactant macromonomers. The polymers showed interesting solution properties, such as enhanced viscosity. Borchardt et.al [21], also reported oil recovery properties of polymer association complexes. Small concentrations of hydrophobically modified polymers such as alkylhydroxyethyl celluloses and associative polymers such as poly(acrylamide-co-N-alkylacrylamide) substantially increased drive water viscosity. Ezzell et.al [23], also investigated the rheological and photophysical evidence for hydrophobic associations in water-soluble polymers. A new fluorocarbon-containing hydrophobically associating polyacrylamide copolymer has also been studied and found to have thickening ability in aqueous solution [24]. McCormick et.al

[26], reported the ability of random and graft copolymers to maintain large hydrodynamic volumes in dilute solutions in the presence of mono and divalent electrolytes and found to be critical for mobility control. Wesslen et.al [27], investigated the preparation and properties of some water-soluble, comb-shaped, amphiphilic polymers. All the polymers were found to be surface active with CMC on the order of 1.5g/l, and surface tensions of 38-45 dync/cm.

In order to develop polymers that are capable of providing simultaneously ultralow interfacial tension and mobility control, three classes of amphiphilic sidechain polymers are considered in this study. The known variables that lead to ultralow interfacial tension in the surfactant solutions, and the studies of associative polymers as mobility controllers will be used to guide the selection and design of the polymers in this study.

## 2.3 RHEOLOGICAL BEHAVIOUR STUDIES

Studies of the rheological behaviour of hydrophobically modified polymers [16–26], can help in guiding the choice of the type and number of groups that need to be incorporated in the polymer molecule to produce aggregates of size large enough to give the required viscosity. Size and molecular weight are related to viscosity by the stokes law and the self-avoiding-walk model [28]. The required viscosity can be calculated from the total relative permeability of the reservoir rock [29].

Viscosity is a measure of the energy dissipated by a fluid in motion as it resists an applied shearing force. The dissipation is a form of friction and, in an adiabatic system, results in an increase in the temperature of the system. This

friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement, which is called "shear". Shearing occurs whenever the fluid is physically moved or disturbed, as in pouring, spreading, spraying, mixing, e.t.c. Highly viscous fluids, therefore, require more force to move than less viscous materials. In laminar, unidirection flow, the term shear stress,  $\tau$ , and the rate of shear,  $\gamma$ , are used to indicate the applied force and the response of the fluid. A certain force per unit area " $f/A$ " is required to maintain a constant-velocity gradient, in this case " $u/y$ ". These quantities of interest are expressed as,

$$\tau = \text{shear stress} = \frac{f}{A} \quad (2.4)$$

$$\gamma = \text{rate of shear} = \frac{u}{y} \quad (2.5)$$

$$\eta = \text{shear viscosity} = \frac{\tau}{\gamma} \quad (2.6)$$

For many liquids of lower molecular weight, Newton's law applies; i.e, the viscosity is a constant independent of the magnitude of  $\tau$  or  $\gamma$ . What this means in practice is that at a given temperature the viscosity of a Newtonian fluid will remain constant regardless of which viscometer model, spindle or speed used to measure it. For many polymer solutions, the shear stress and shear rate are not proportional over all ranges, so that the non-Newtonian viscosity as defined by equation (2.6), is not a constant. In other words, when the shear rate is varied, the shear stress doesn't vary in the same proportion (or even necessarily in the same direction). The viscosity of such fluids will therefore change as the shear

rate is varied. Thus, the experimental parameters of viscometer model, spindle and speed all have an effect on the measured viscosity of non-Newtonian fluid. This measured viscosity is called the "apparent viscosity" of the fluid and is accurate only when explicit experimental parameters are furnished and adhered to.

Non-Newtonian flow is probably a mechanical proposition. As non-symmetrical objects pass by each other, as happens during flow, their size, shape, and cohesiveness will determine how much force is required to move them. At another rate of shear, the alignment of the objects may be different and more or less force may be required to maintain motion. By non-symmetrical objects, large molecules, colloidal particles, and other suspended materials such as clays, fibre, and crystals are referred to. There are several types of non-Newtonian flow behaviour, characterized by the way a fluid's viscosity changes in response to variations in shear rate. The most common types of non-Newtonian fluids encountered include Pseudoplastic, Dilatant, Plastic, Thixotropy, and Rheopexy. Pseudoplastic fluid displays a decreasing viscosity with an increasing shear rate. This type of flow behaviour is sometimes called "shear-thinning". Dilatant displays increasing viscosity with an increase in shear rate. Dilatancy is also referred to as "shear-thickening" flow behaviour. Plastic type fluid behaves as a solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced; this force is called the "yield value." Thixotropic fluid undergoes a decrease in viscosity with time, while it is subjected to constant shearing. Rheopexic fluid displays the opposite of thixotropic behaviour, in that the fluid's viscosity increases with time as it is sheared at a constant shear rate. Both thixotropy and rheopexy may occur in

combination with any of the previously discussed flow behaviours, or only at certain shear rates. The time element is extremely variable; under conditions of constant shear, some fluids will reach their final viscosity value in a few seconds, while others may take up to several days. [30,83].

Schulz et.al [31], reviewed some work on the rheological measurements and preparation, characterization and rheological behaviour and properties of some water-soluble polymers.

Apart from the ability of hydrophobically modified associative polymers to substantially increase drive water viscosity, they also showed unusual dependence on concentration as compared to conventional polymers [16–26]. McCormick et.al [4], studied the synthesis and aqueous solution behaviour of associative acrylamide/N-alkylacrylamide copolymers (water-soluble copolymers) and observed the polymers to show a remarkable increase in apparent viscosity at low mole fractions of the N-alkylacrylamide in the copolymer. Wang et.al [17], observed a substantial increase in viscosity of hydrophobically modified poly(sodium acrylate), an ionic polymer when sodium chloride (NaCl) was added to the aqueous polymer solution. The same observation was made when hydrophobically associating polymers containing N-vinyl-pyrrolidone functionality was dissolved in an aqueous brine solution. The polymers have the ability to substantially increase the viscosity of the aqueous solution [16]. The initial increase in viscosity could be attributed to the screening of the charge repulsion among the polymer main chains, which probably promoted more interchain association and actually causing the increase in the viscosity. The decrease in the viscosity with further addition of sodium chloride could be due

to the formation of compact networks micelles beyond a certain value of salt concentration [17].

In another study a decrease in solution viscosity of hydrophobically modified polymer was observed upon the addition of a surfactant solution [4]. Apparently the added surfactant solution associated with the hydrophobic segments on individual polymer molecules, thereby leading to suppression of the intermolecular association of the polymers [1]. This observation is not in favour of mixing surfactants with hydrophobic polymers in enhanced oil recovery as previously discussed in chapter 1. Other hydrophobic polymers studied include acrylamide-surfactant copolymer [18], sulfonated styrene-butyl-styrene block copolymer [19], alkylhydroxyethyl ethyl celluloses [21], N-(4-butyl)phenylacrylamide and sodium-3-acrylamido-3-methylbutanoate (NaAMB), [22], and copolymers of acryl-amide with sodium-2-acrylamido-2-methyl-propane sulfonate (NaAMPS), [26]. All these showed remarkable increase in viscosity and less sensitivity to salts.

## **2.4 SURFACE AND INTERFACIAL TENSIONS BEHAVIOURS STUDIES.**

Bektruov et.al [32], reviewed hydrophobically associating polymers, studied as polymeric surfactants or polysoaps, because their amphiphilic character make them surface active. Most of the work on this subject were concentrated on the measurement of water solubility, solution viscosity measurement and solubilization of hydrocarbon [33]. Ultralow interfacial tension in surfactant systems is usually associated with the formation of a middle phase microemulsion. Winsor [34], referred to this phenomenon as type III phase diagram. Micellar two-phase systems have also exhibited an ultralow interfacial



tension [35]. The very low interfacial tension in surfactant systems has been attributed to the balance between the hydrophobic and hydrophilic forces on the surfactant molecules, which cause the molecules to concentrate at the interface and lower the interfacial tension. This idea has been quantified by defining a quantity "R", which is defined as the ratio of solvent attraction between surfactant and oil to solvent attraction between surfactant and water, and can be expressed as, [36],

$$R = \frac{\Lambda_{co}}{\Lambda_{cw}} \quad (2.7)$$

Other interactions have been included in the definition of "R" [34,36]. The value of "R" has to be very close to unity before a middle phase microemulsion and hence ultralow interfacial tension could be obtained. Such external variables as temperature, salinity and oil type have influence on the value of "R". The value of "R" is also influenced by the internal variables such as the structure of the surfactant molecules and the nature and relative size of the hydrophilic and hydrophobic groups [37 – 53]. Therefore, for a given set of external variables (i.e temperature, salinity e.t.c), the concept of hydrophilic and hydrophobic balance (i.e  $R = 1$ ) can be applied to guide the choice of hydrophobic and hydrophilic groups added to a given polymer solution. It must be remembered, however, that, as has been noted, R may vary from point to point because of the thermal fluctuations in concentration within the solution, so that, in practice, unlimited extension of the micelle may not occur, even in the range of relative concentrations where the mean value of R is unity. In certain circumstances, however, the thermal fluctuations are not sufficient to disrupt long-range order,

and a stable lamellar (i.e  $R = 1$ ) arrangement of hydrophobic, amphiphilic and hydrophilic layers may still persist. Where the mean value of  $R$  is  $< 1$  or  $> 1$ , the affinity of the surfactant layer is no longer the same for the oil and water regions. The surfactant layer will tend to become convex toward the water region for  $R < 1$ , since this inequality implies that the relative miscibility of the surfactant layer with the water region has increased and/or that with oil region has decreased. This tendency for the interface to curve can also be visualized by imagining that when  $R \ll 1$ , the tendency will be to maximize the interfacial area of contact with water region while minimizing it with the oil region [36].

Amphiphilic compounds tend to concentrate as a monolayer at a water/oil interface, with the tendency increasing as both the hydrophobic and hydrophilic character of the amphiphile become more pronounced. At the interface, amphiphilic compounds are arranged so that the hydrophobics are removed from the water while the hydrophiles remain in contact with the aqueous solution. This molecular orientation is consistent with a number of experimental observations, including the sharp reduction in surface or interfacial tension attending the addition of small quantities of amphiphile to an aqueous phase. Because of this pronounced tendency for amphiphiles to accumulate as a monolayer at an interface, and there to reduce the surface tension, they are sometimes called surface-active agents or, more simply, surfactants [36]. A surfactant molecule contains at least one polar hydrophilic part and at least one apolar hydrophobic unit, such as a hydrocarbon chain. Typical examples are soaps (i.e sodium alkanoates) or phospholipids which form membranes. The coexistence of two opposite types of behaviour (i.e hydrophilic and hydrophobic) inside the same molecule is the origin of local constraints which lead to

spontaneous aggregation into labile structures, such as micelles and lamellae observed with surfactants in solution of oil or water. Micellar aggregation can be demonstrated by measurements of physical properties against surfactant concentration. The most significant property is surface (or interfacial) tension (figure 2.1) . As surfactant concentration is increased, surface tension is lowered because of adsorption of surfactant at the surface. The higher the concentration, the larger the adsorption (adsorbed molecules are in equilibrium with bulk dissolved ones) and lower the surface tension. This surface tension decrease occurs up to a well defined concentration which is called critical micellar concentration (CMC). Above it, tension remains nearly constant, which expresses an almost constant concentration of molecularly dissolved molecules (monomers). The excess molecules aggregate into micelles, in equilibrium with monomers. The word "micelle" refers to aqueous solutions (direct micelle), micellar aggregation in apolar solvents occurs in "reverse" or "inverted" micelles [83]. This phenomenon is shown in figure 2.1 .

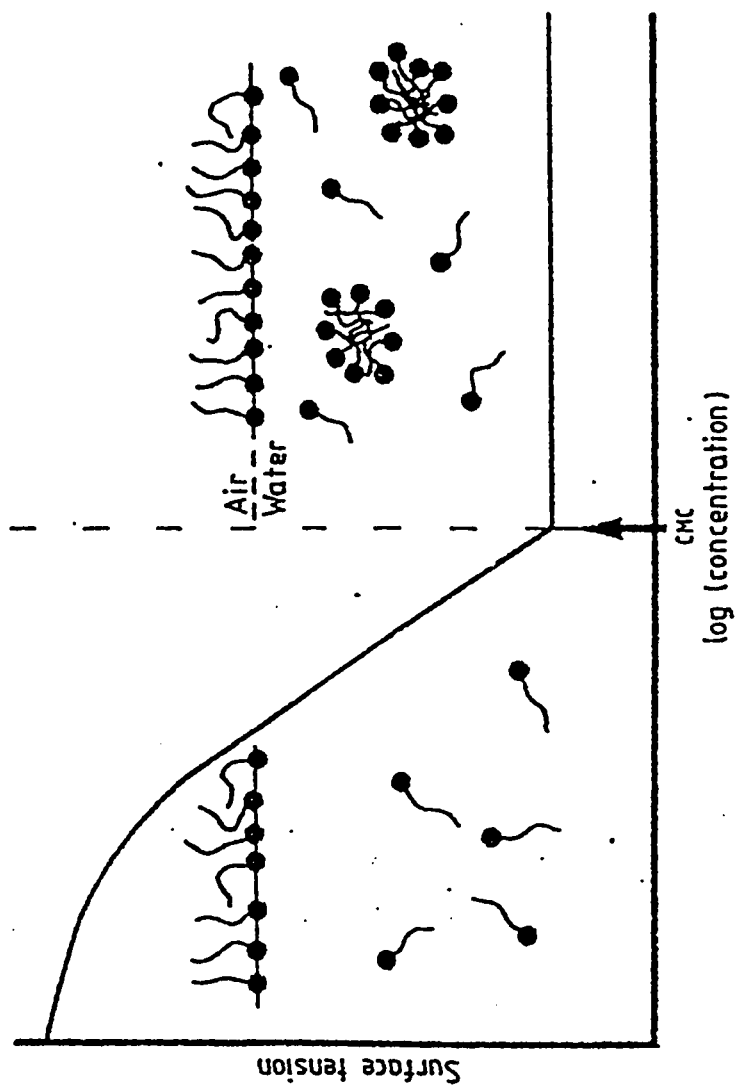


Figure 2.1. Surface (air-water) tension as a function of surfactant concentration for an aqueous micellar solution.

The task of designing a polymer with both low interfacial tension and high viscosity is not a simple one. However, the following observation gives high promise of success. Hamad et.al [49], established the ability of amphiphilic sidechain polymers to reduce the surface tension in a study of the solution behaviour of a comb-like commercial polymer Dapral GE-202-Na. The copolymer of maleic anhydride alpha-olefin with hydrophilic ester and ether groups (  $\text{CH}_2 - \text{CH}_2\text{O}$  ), hydrophobic alkyl sidechains (  $\text{CH}_3(\text{CH}_2)_9$  ) and ionic carboxyl groups. The air-water surface tension of this polymer solution was observed to drop sharply at low concentration and then remains constant with further increase in polymer concentration. This is similar to what is normally observed for surfactant solutions. Although surfactants give an air-water surface tension of around 20 dyne/cm, they do give ultralow oil-water interfacial tension at the optimum conditions of salinity, temperature etc [1]. Similar behaviour is expected for surface active polymers such as amphiphilic polymer, because they are simply surfactant molecules bonded together [1]. Unfortunately most of the surface tension studies in the literature were conducted on polymers at the air-water interface [37–53]. However a study of the interfacial tension between two aqueous phases in the presence of polymer has been conducted, [40,42], but it is not relevant to the present work i.e the study of interfacial tension at the oil-water interface. The literature on the interfacial tension at the oil-water interface of the hydrophobically modified associative polymers is still lacking.

Chou et.al [5], established the superiority of the oligomeric surfactants to conventional surfactants in lowering the interfacial tension. These molecules also

enhanced the aqueous solution viscosity to about 100 cps, more than what is expected from the conventional surfactants. It has also been observed that polymers have the ability to lower the interfacial tension between two organic liquid phases by one to two orders of magnitudes [41]. The same study also showed that increasing the molecular weight, decreases the interfacial tension, and since the viscosity is known to increase with the molecular weight [28], this result then shows that achieving ultralow interfacial tension and high viscosity, simultaneously is possible.

Wesslen et.al [27], studied the properties of some water-soluble, comb-shaped, amphiphilic polymers and established that all the polymers studied were surface active with CMC on the order of 1.5g/l, and surface tensions of 38-45 dyne/cm. Surface tension of polyacrylic acid has also been measured in sodium chloride solutions at various ionic strengths. Surface active property of polyacrylic acid solutions increases and shows a large time dependence with increasing concentration [51,52]. Ananthapadmanabhan [53], established that a new class of water-soluble cellulosic polymers exhibits definite surface active property at air-liquid and liquid-liquid interfaces. The hydrophobic modified polymers clearly showed more surface active property than the unmodified polymer. The surface active property of the modified polymers is only moderate compared to that of conventional surfactants which exhibit ultimate surface tension values in the range of 20-40 mN/m.

## 2.5 POLYMER SYNTHESIS AND MODIFICATION STUDIES

Two classes of polymerization reactions and a polymer modification are considered in this research. The reactions are, the copolymerization of 1-alkene

(alpha olefin) with maleic anhydride, the cyclopolymerization and cyclocopolymerization of diallylamine derivatives and modification of the urethanized polyvinylalcohol (PVA).

### **2.5.1 Copolymerization of 1-alkene with Maleic anhydride.**

Maleic anhydride is a powerful electron acceptor and has been widely used as a comonomer in alternating copolymerization. In common with many of these strong donor and acceptor molecules, it is difficult to homopolymerize, but enters into a copolymerization reaction with considerable ease when the comonomers are donors [55]. A number of olefins, ethylene, cis-butene-2-, trans-stilbene, allylacetate, undergo alternating copolymerization reaction with maleic anhydride. The reaction with ethylene, under pressure, and in the presence of benzoyl peroxide, has been described in detail [55], and this procedure can also be applied in general to propylene, 1-dodecene, 1-hexadecene, vinyl acetate, methyl ether, and styrene. Infact that of styrene with maleic anhydride in the presence of dibenzoyl peroxide has also been described in detail [57]. Alternating copolymers involving substituted maleic anhydrides and olefins have also been reported [58 – 60].

Furthermore it has been found that terpolymers of maleic anhydride, with atleast one lower-1-alkene and atleast one higher 1-alkene in specified monomer ratios, have desirable waxy properties enabling them to be used in a variety of end uses, that include viscosity characteristics, which enable the polymers and products containing the polymer to flow [61]. In the same study, it has been found that the incorporation of a lower 1-alkene as a termonomer in a polymer of maleic anhydride and higher 1-alkene increases the solubility of the resulting

polymers and reduces the viscosity of solutions of the polymer, but does not substantially change the waxy properties of the maleic anhydride higher 1-alkene copolymers [61]. Alternating copolymers of maleic anhydride have also been reported to show high surface active property. Most especially effective are maleic anhydride (acid and/or salt) copolymers with a relatively hydrophobic comonomer such as an alkyl vinyl ether [62].

### **2.5.2 Modification of Urethanized Polyvinylalcohol (PVA).**

Polyvinylalcohol can be modified by esterification reaction. If the added sidechain has carboxyl functional group, then they can be attached to the polymer main chain through the ester linkage or the more stable amide or ether linkage. To form the amide linkage, the amine of the desired hydrophobic group is reacted with carboxyl group in a specific environment. This reaction has been used to attach small amounts of octadecyl chains to polyacrylic acid with a reported yield of almost 100 percent [17]. To form the ester linkage the alcohol of the desired hydrophobic group is reacted with the carboxyl groups of the polymer. To make the reaction goes faster and increase the yield, the carboxyl group can first be reacted with thionyl chloride to form the highly reactive group "COCl", which readily reacts with alcohols to form esters. The two steps are essentially irreversible and give almost 100 percent yield. Furthermore, if it is desired to increase the hydrophilicity of the polymer without ionic groups to avoid possible sensitivity to salt concentration, a polymer with the hydroxyl groups can be reacted with ethylene or propylene oxides to form ethoxylates or propoxylates.



Sakurada et.al [63], established that partly urethanized polyvinylalcohol (PVA) is more soluble than original polyvinylalcohol in solvents such as water, dimethylformamide, and dimethylsulfoxide at room temperature. Moreover, the aqueous solution of partly urethanized polyvinylalcohol is more stable than an aqueous solution of the original polyvinylalcohol. Partly urethanized polyvinyl alcohol can be obtained [64], by treatment of polyvinylalcohol with urea. The solubility of this polymer in water is a function of the degree of substitution: highly substituted polymer is soluble in organic solvents, but less substituted polymer is soluble in water, giving a stable solution. Such a change in solubility may be due to the irregularity in the chain structure owing to the introduction of bulky O. CO. NH<sub>2</sub> residue. The C = O and NH in the side residue are capable of forming hydrogen bonds with NH and C = O, respectively, in addition to hydrogen bonds originating from OH groups. Accordingly, in more highly urethanized polyvinylalcohol, C = O, may strongly be hydrogen bonded to NH of the same or different polymer chain; thus the solubility in water may be remarkably reduced.

Reactions of the acid chlorides of long-chain acids, and of other derivatives, with polyvinylalcohol have also been investigated, mainly with the objective of producing materials of potential utility in surface coatings and, in some cases, for substrate materials for photographic system [65,66].

Polyvinylalcohol is used mainly when dissolved in water. Its solubility in water depends on its degree of polymerization and degree of hydrolysis: the effect of the latter is especially significant, its many hydroxyl groups cause it to have high affinity to water, with strong hydrogen bonding between the intra-and

intermolecular hydroxyl groups, greatly impeding its solubility in water.

On the other hand, the residual acetate groups in partly hydrolysed polyvinylalcohol are essentially hydrophobic, and thereby weaken the intra-and intermolecular hydrogen bonding of adjoining hydroxyl groups. The presence of an adequate amount of these acetate groups increases the water solubility [67]. In view of this, attempt was made to further hydrolyze the original PVA with molecular weight of 100,000 in order to make it almost 100 percent PVA. Bravar et.al [68], studied the alcoholysis of poly(vinylacetate) to polyvinylalcohol and observed the polymers to show an increase in the extent of hydrolysis proportional with the increase of intrinsic viscosity values of fractions. McDowell et.al [69], and Sakurada et.al [70], also established the same trend in their studies.

### **2.5.3 Cyclopolymerization and Cyclocopolymerization of Diallylamine Derivatives.**

The formation of cyclic structures in the polymer chain from acrylic monomers and comonomers during the polymerization process was first discovered in the early 1950's. During the next 20 years several interesting cyclopolymerization systems have been developed and their mechanism of cyclization investigated as reported by cotter et.al [71]. However, the one system that has the greatest industrial potential and utilization is that of diallylammonium halide. This polymer alone accounts for over 200 patents and publications. Extensive industrial research on the homopolymerization and copolymerization of diallyl ammonium salts with potential commercial utilization is being carried out. Butler et.al [72], patented the

cyclopolymerization of symmetrical diallylammonium chloride and bromide salts. Originally, the polymerization reaction was initiated by tert-butylhydroperoxide, azobisisobutyronitrile, or peracetic acid and carried out at 50 – 80°C in polar solvents such as water or dimethylformamide. Butler et.al [73], reported that polymers obtained from the chloride salt of the monomer had significantly higher intrinsic viscosity than those from the bromide salt. Comparing the polymers obtained from dialkyldiallyl ammonium salts in dimethylsulfoxide initiated by ammonium persulfate to those obtained from the tert-butylhydroperoxide-water system. Negi et.al [74], confirmed Butler's findings that the quaternary ammonium chlorides polymerizes more readily and produces higher molecular weight polymers than the bromide salts. The inhibition of polymerization was attributed to the ease of oxidation of the bromide ion by the persulfate which can result in both the consumption of the initiating species and generation of bromine which can terminate the growing chain.

Boothe et.al [75], in an investigation of the factors affecting the homopolymerization of dimethyldiallylammonium chloride reported that polymers with the highest solution viscosity and lowest residual monomer content were obtained from a 65% monomer solution catalyzed by ammonium persulfate. They also found that the addition of 200 ppm of sodium ethylenediaminetetraacetate (  $\text{Na}_4\text{EDTA}$  ) improved the rate as well as the degree of polymerization. It was also found that extremely monomer purity was necessary to obtain a high molecular weight polymer. If the monomer was contaminated with even small amounts of allyl alcohol or dimethylamine, the

polymer molecular weight was reduced. Consequently, preparation of a high-purity monomer by careful control of the synthesis reaction [76], and purification steps [77], is essential to remove these chain-transfer agents and other impurities.

The diallyl quaternary ammonium monomers have also been copolymerized with a number of monomers to produce a variety of cationic copolymer; an example is the cyclocopolymerization of diallylammonium compounds with sulfur dioxide to produce water soluble cationic polysulfones. These copolymerizations have been carried out in solvents such as dimethylsulfoxide, methanol and acetone with free-radical initiators such as ammonium persulfate, ammonium nitrate, azobisisobutyronitrile, tert-butylhydroperoxide, and dilauroyl peroxide [78 – 80].

### CHAPTER 3

#### EXPERIMENTAL SET-UP AND PROCEDURES FOR MEASUREMENTS.

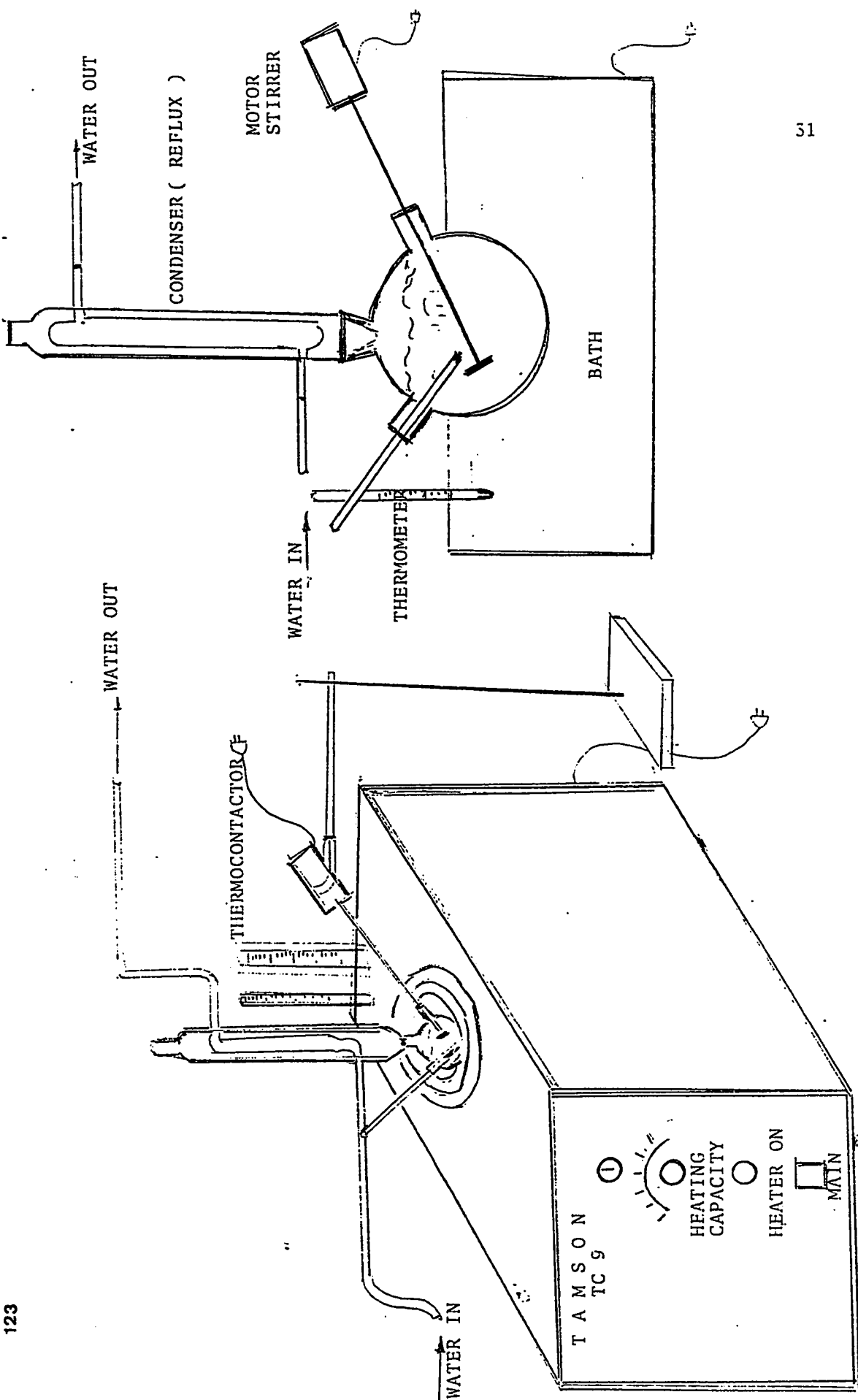
Most of the reactions carried out in this research were performed in the experimental set-up shown in figure 3.1. In this set-up, appropriate amount of monomers or reagents and initiators are placed in a multiple-necked or ordinary flask, fitted with stirrer, stoppers, thermometer and reflux condenser. The reaction mixture is then stirred and maintained at the temperature and pressure conditions of the reacting mixture till the end of the reaction. Rheological behaviour studies are performed using a Brookfield digital rotational viscometer with coaxial cylinder measuring system and temperature controller, hooked to a data acquisition computer system. Surface and interfacial tensions are measured by a processor tensiometer K12 (plate and ring methods).

#### 3.1 PRINCIPLES AND DETAILS OF THE EXPERIMENTAL SET-UP

##### 3.1.1 Reaction Vessels For Polymerization Reactions

The reaction vessel that was used for most of the polymerization reactions consists of normal multi-necked flasks (e.g three-necked flask) fitted with a suitable high-speed stirrer or magnetic stirrer, thermometer and reflux condenser. The thermometer is used to measure the temperature of the reacting mixture during the course of the reaction and reflux condenser is necessary in order to condense back the vapors that might have escaped from the reaction vessel during the reaction process. High speed stirrer is required for proper and uniform mixing of the reacting mixture.

Exact temperature control is very important in polymerization reactions since, amongst other things, the rate and degree of polymerization are strongly dependent on temperature. For accurate work, a water or paraffin oil bath, whichever is appropriate is used, thermostatted in the normal way with the aid of a contact thermometer and immersion heater. This set-up is shown in figure 3.1.



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Fig. 3.1 : . The Reaction Vessel for Polymerization Reactions-Schematic

### **3.1.2 The Brookfield Digital Viscometer ( Model DV-II ) with Data Gathering Program "DV Gather"**

The Brookfield thermal system consists of a Brookfield viscometer, with related accessories, such as spindles, a narrow guard leg and other accessories as shown in figure 3.2. Viscosity measurements are obtained using coaxial cylinder geometry. The temperature is controlled by a solid state, triac output, proportioning controller which maintains the spindle, chamber, and sample material at the desired temperature. The system is designed for measuring liquid viscosities over a temperature range of up to 300°C ( 572°F ). The low limit of temperature control is 15°C ( 27°F ) above ambient temperature. The designed viscosity range is from 1 cps to 8,000,000 cps depending upon the viscometer, SC4 and UL adapter spindles utilized.

The Brookfield UL adapter accessory has been developed for use with the Brookfield viscometers to allow accurate and reproducible viscosity measurements to be made on low viscosity materials, as low as 1 cps. At 60 RPM, the LVT model has a full scale range of 1-10 cps with the UL adapter. The UL adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube. Its rheological correct cylindrical geometry provides extremely accurate viscosity measurements and shear rate determinations. The tube has a removable end cap. With the cap removed the open ended tube can be used in a beaker or tank. With the cap in place the closed tube holding a 16 ml sample can be immersed in a temperature bath. Working temperature range is from -10°C to 100°C. All immersed parts are stainless steel. The removable cap of low density polyethylene can be considered disposable for one-time use if



required. The Brookfield viscometer is guaranteed to be accurate within 1.0 % of the range in use. It also has a sensitivity and reproducibility of 0.2% .

The Brookfield digital viscometer, model DV-II, is a laboratory viscometer which can be utilized with all Brookfield accessories including UL adapter, small sample adapter, thermosel and helipath stand. Also available with the instrument are; continuous display of basic viscometer reading in %, continuous display of calculated shear stress in  $\text{dyne/cm}^2$ , AutoZero for automatically zeroing the viscometer, AutoRange for displaying full scale viscosity and shear stress range of any spindle/ speed combination, and for verifying special spindle entries, Hold for freezing any display reading, low indicator for readings below 10% of full scale range; programmed to accept all Brookfield spindles and spindle/chamber accessories.

The Brookfield digital viscometers rotate a sensing element in a fluid and measure the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, which is called a spindle, through a beryllium copper spring. The degree to which the spring is wound, detected by a rotational transducer, is proportional to the viscosity of the fluid. Continuous readouts of percent full scale, viscosity and shear stress are provided by means of the integral three-digit LED display. The minimum viscosity range is obtained by using the largest spindle at the highest speed; the maximum range by using the smallest spindle at the slowest speed.

The data gathering program (software) is an easy-to-use, menu-driven program developed to facilitate data gathering and rheological analysis. It is

designed for use with all models and accessories of the Brookfield DV-II calculating viscometer.

# Brookfield Thermosel System 1

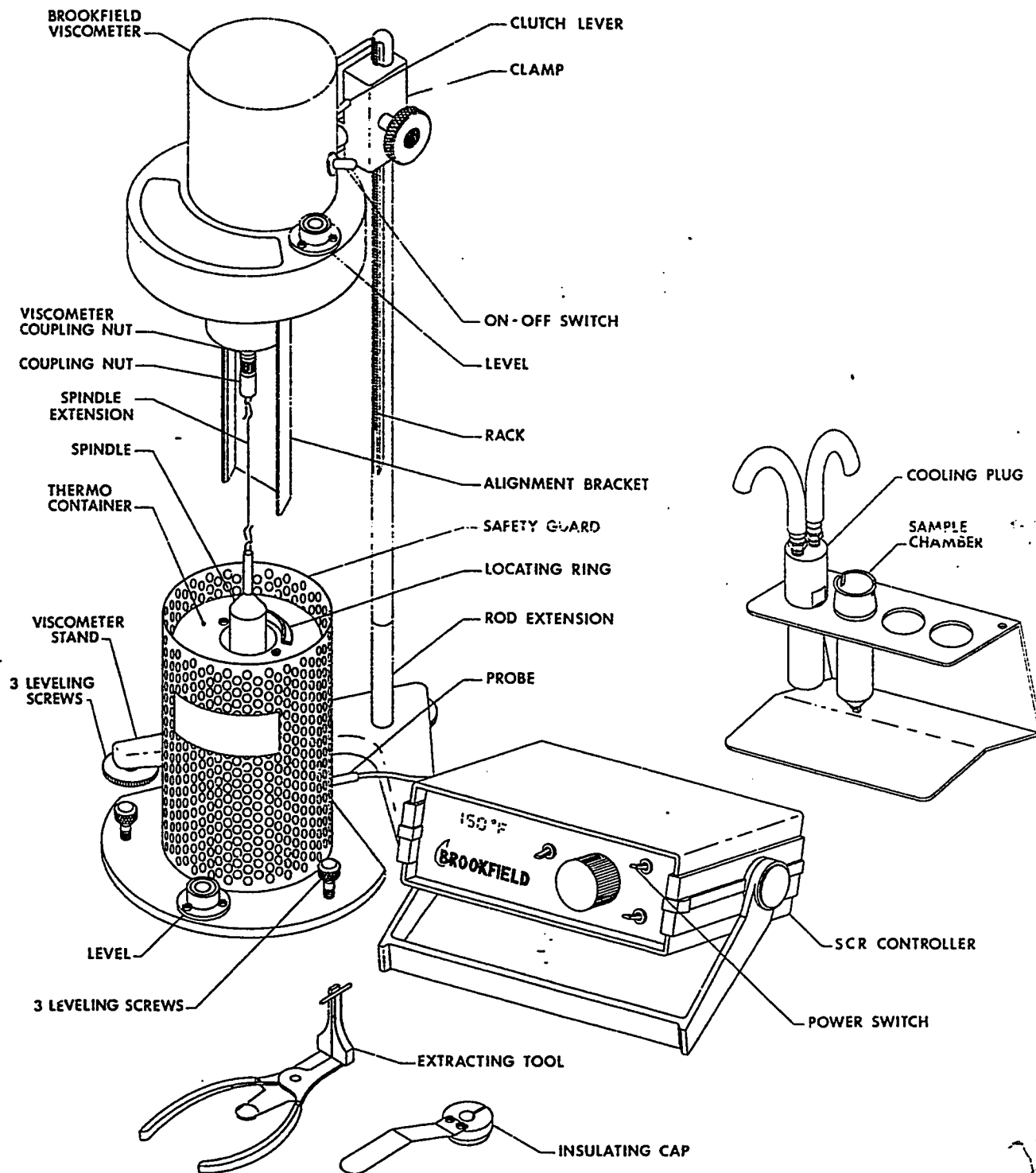


Figure 3.2: The Brookfield Digital Viscometer (Model DV-II).

### 3.1.3 Interfacial and Surface tension Measuring Instruments

The tensiometer consists of a measuring instrument and a processor control unit. The balance system situated in the head part of the instrument has an accuracy of 0.0001g and 0.01mN/m respectively. It incorporates a servosystem for fully automated calibration and taring. The solid metal housing provides the instrument with great stability and shock resistance; therefore a weighing table is usually unnecessary. Due to the rigid connection of the ring or plate to the balance system, a measurement is possible in both push and pull direction. A measurement in the push direction is necessary whenever the lighter phase has a higher affinity to the measurement body (ring or plate) than the heavier phase. The temperature of the sample is optionally controlled using a circulator bath, measured by the built-in pt-100 thermoresistor, and is displayed digitally. The force which is detected when a measuring device of known circumference is moved into the interface of two immiscible phases (liquid/liquid or liquid/gas) is directly proportional to the surface and interfacial tensions between these phases

$$\sigma \approx \frac{F}{L} (\text{mN/m}) \quad (3.1)$$

Depending on the individual needs, the platinum ring or the platinum plate are used as the "force pick up".

To minimize temperature changes and air circulation, plexiglass doors have been installed to isolate the measuring area. Yet complete access is possible by just opening the doors. Integrated in the thermostat vessel is a magnetic stirrer, which can be operated either manually or automatically by the processor. This feature generates reproducible starting conditions when measuring samples of

the same solution at different concentrations. The combination of an electronic balance system and a processor control unit enables fully automated measurements. There is no further need to correct the values obtained by the plate method. The processor tensiometer K12 takes care of this job.

### 3.1.3.1 The Ring Method.

The measuring device is a platinum ring which is suspended horizontally for the measurement. The geometry of the ring has to be known. It determines the wetting length  $l_b = 119.95$  of the ring, calculates the means radius  $R = 9.545$  mm and the radius of the cross-section of the wire  $r = 0.185$  mm (for the standard kruss-ring)

The platinum ring is dipped into the sample liquid and immediately removed afterwards as shown in figure 3.3. The maximum force  $k_{\max}$ , which is necessary to pull the wetted circumference  $l_b$  of the ring through the surface of the liquid is measured

$$\sigma = k_{\max} \frac{\Gamma_{\text{ef}}}{l_b} \quad (3.2)$$

The correction factor takes into account the weight of the liquid which is lifted by the ring into consideration. The main disadvantage of the ring method is the necessity of correction of the measured values. It does not only determine the force on the ring caused by the surface tension but also the weight force of the liquid volume of the lamella at the bottom of the ring as shown in figure 3.3. The automatic correction of the processor tensiometer K12 was based on publication of Zuidema et.al [81]. The equation was interpolated using the tables

of Harkins et.al [82].

### 3.1.3.2 The Plate Method.

The measuring device is a vertically suspended platinum plate of exactly known geometry. The surface of the plate is roughened for better wetting property. The lower edge of the plate is brought into contact with the sample liquid. The liquid "jumps" to the plate and pulls the plate into the liquid. The force  $K$ , caused by this wetting is measured by pulling out the plate up to level of the liquid surface as shown in figure 3.3.

The measuring procedure is static, which means that the plate can stay at zero level for a long period. Thus a continuous measurement of the surface tension is possible, without the problem of forming a new surface all the time as it is necessary with the ring method.

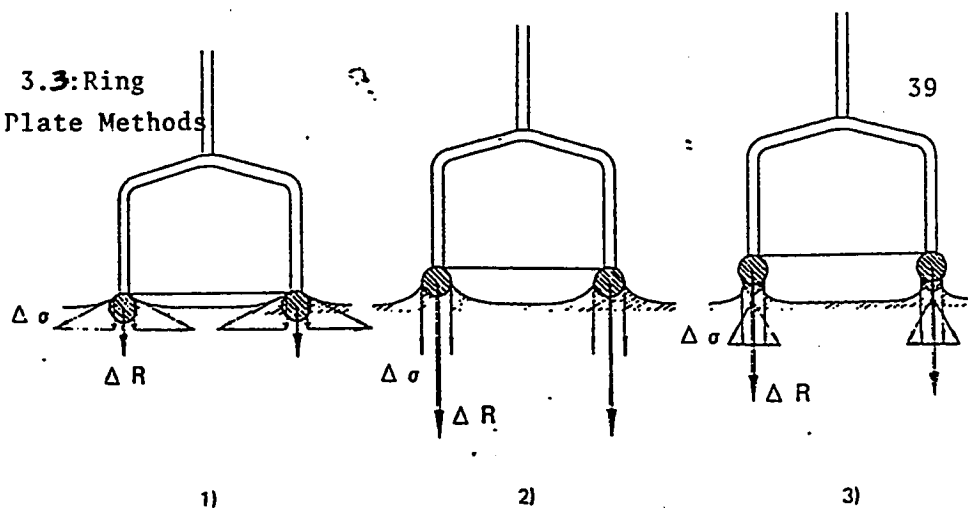
The measured values do not need a correction, which is another advantage of the plate method. The surface tension of the liquid is determined according to the wetted length  $l_b$  as

$$\sigma = \frac{K}{l_b \cos \theta} \quad (3.3)$$

Equation 3.3 for the determination of the surface tension can only be used if the contact angle is 0 and therewith  $\cos \theta = 1$ , which implies total wetting of the plate. This condition is complied with the roughened and clean platinum plates, which are usually used for the measurement.

Separate stages in measurement with the ring (the ring is shown in section)

Fig. 3.3: Ring and Plate Methods



Parallelogram of forces acting on a cross-section element with respect to lamella height.

The force  $\Delta \sigma$  is related to the surface tension  $\sigma$ . During measurement, the point of application and the direction of the force will change but the resultant remains a constant.

$\Delta R$  is proportional to the measured force  $K$  (see equation (1))

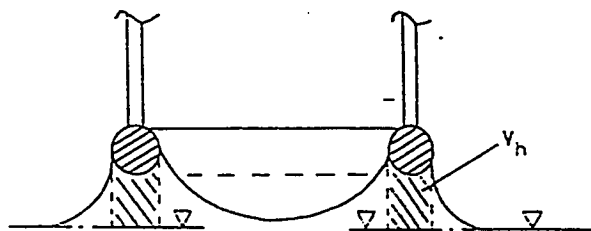
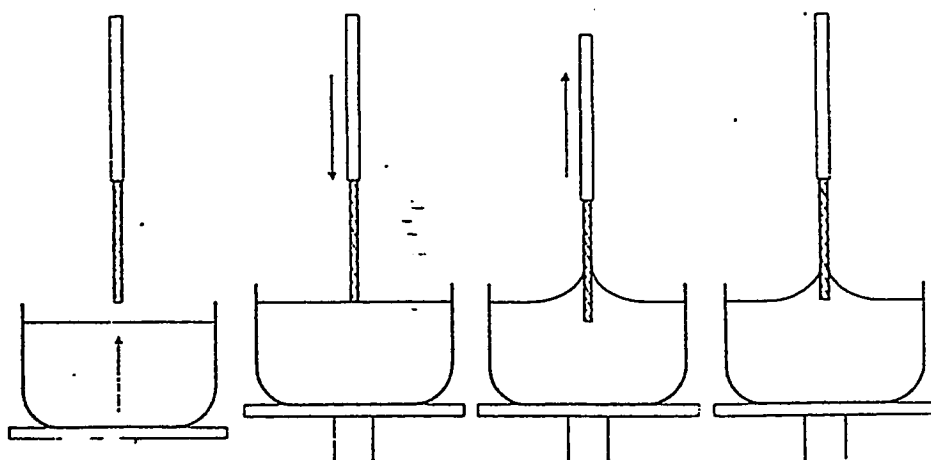


Fig. 24: Ring with liquid-lamella in a real system (cross sectional view of the ring)

Separate stages in measurement with the plate (the plate is shown in section)



Test vessel is raised towards the lower edge of the plate.

The lower edge makes contact and the plate is drawn into the liquid by surface tension.

The plate is drawn up to the zero level by the tensiometer.

### **3.2 PROCEDURES FOR VISCOSITY AND SURFACE AND INTERFACIAL TENSIONS MEASUREMENTS.**

Rheological behaviour studies were performed by using a Brookfield digital rotational viscometer with coaxial cylinder measuring system and temperature controller. Surface and interfacial tensions were measured by plate and ring methods tensiometer.

#### **3.2.1 Viscosity Measurements**

The instrumentation was placed on a firm level surface. The viscometer stand was set up by connecting the rod extension to the bottom of the upright rod. Then the assembly part (upright rod and rod extension) was screwed into the base, leaving the jam nut loose. The three leveling screws were then screwed into position on the base. The viscometer was then attached to the stand by inserting it into the clamp, and positioning it reasonably level and centered between the stand legs. The assembled part (upright rod and rod extension) was locked tightly to the stand base with the jam nut. The viscometer was then raised to the highest position on the stand as shown in figure 3.2. With the viscometer raised to the highest position on the stand, the alignment bracket was then attached to the rear of the viscometer pivot cup, securing it tightly with the knurled screw. With the use of the three leveling screws in the thermo-container base, the base level was positioned. The chamber was then inserted into the thermo-container using the extracting tool. The chamber was rotated until it drops and locks in place prohibiting further rotation.

The temperature controller was then set on a level adjacent to the right of



the thermo-container as shown in figure 3.2. The male plug ( three-prong) was then inserted from the thermo-container braided cord into the socket on the back of the container. The four-inch stainless steel probe was inserted into the hole in the thermo-container located directly above the braided cord. The other end of the probe was then plugged into the connector located on the back of the controller.

By looking down on the viscometer, the stand base was leveled by adjusting the three leveling screws until the bubble is centered. The viscometer was then lowered until the tips of the alignment bracket just touch the horizontal surface of the locating ring. The viscometer was then raised, positioning the tips of the alignment bracket about 1/16 inch above the horizontal surface behind the locating ring. Using both hands, the thermo-container base was gently slid until the tips of the alignment bracket just touch the locating ring. The coupling link was then connected to the spindle and to the coupling nut. The spindle was lowered into the chamber and the link coupling nut was connected on to the viscometer coupling nut using the left-hand thread. The insulating cap was then placed over the sample chamber inlet, thus capping the system. The whole set-up is shown in figure 3.2.

With the instrumentation assembled and familiarization completed, the viscosity measurement can now be performed as follows. First of all, the insulating cap and spindle were removed. The viscometer was then raised to the highest level on the stand. The sample chamber was removed, using the extracting tool, and was placed in the auxiliary holder. By the use of pipette, the appropriate volume of polymer solution designated on the range data sheet was

poured into the sample chamber. Using the extracting tool, the loaded chamber was put back into the thermo-container. The viscometer was then lowered and the thermo-container was properly aligned. The appropriate spindle was then inserted into the polymer solution in the chamber and was coupled to the viscometer. The insulating cap was then replaced.

The controller was turned on and the set point knob adjusted to the desired set point temperature at which viscosity measurements are to be made. After this, the viscometer was also turned on and left running during the equilibrium period. After the thermo-container, spindle, chamber, and the test polymer solution sample reached temperature equilibrium, which took about 30 minutes, viscosity readings were then taken at different speeds, shear stress and shear strain and viscosities were then obtained at different temperatures and shear rates.

### **3.2.2 Surface and Interfacial tensions Measurements**

#### **3.2.2.1 Ring Method.**

Before measurement was carried out, the ring was cleaned with acetone and distilled water and annealed shortly to red-hot using bursen burner. The ring was then fixed into the measuring unit. This was done by sliding carefully into the guiding mechanism, situated at the top part of the measuring area. The guidance of the clamping device was locked by turning the small wheel on the left outside of the measuring unit housing clockwise.

For series of measurements, after switching on the instrument, the first menu was displayed: And from this, the option ring method was pressed.

Subsequently surface tension and series of measurements options were chosen from the menu displayed. After all these, the sample number, maximum number of measuring values and other preset values were entered. After the polymer solution and the ring were inserted into the measuring unit, the start button was pressed. The fully automatic measuring series begins after pressing START. The end of the measurement was indicated by an acoustical signal. After this, the STOP button was pressed to terminates the reading.

In the interfacial tension measurement, the liquid decane was used as the light phase or oil phase . The same procedure was followed as in the surface tension. In this measurement, two techniques for the force measurement at the interface of two liquids are available; The measurement in pull direction and the measurement in push direction. Both techniques were applied. For the measurement in pull direction, the ring and series of measurement options were chosen from the menu displayed. The sample number, density of heavy phase (polymer solution) and that of light phase (decane) were entered. After this the light phase (Decane) was inserted and the ring was dipped in. The light phase was filled into the sample vessel and the ring was dipped in 2-3 (mm) by lifting up the sample vessel. The taring was started by pressing START. After this, the light phase was removed and the ring was cleaned. The heavy phase (polymer solution) was then inserted and the ring dipped in covered with decane. The fully automatic measurement was then started after pressing START.

Measurement in push direction was started by choosing the appropriate options as done for the case of pull. All the required parameters were then entered and the heavy and light phases were inserted with the ring dipped into

the light phase (Decane). The heavy phase (polymer solution) was filled in up to 6-10 (mm). Then the light phase (about 1 cm height) was carefully overlayed by using a pipette. The ring was dipped into the lighter phase by lifting the sample vessel up. The fully automatic measurement started after pressing START. The STOP button was pressed at the end of the measurement. In this measurement (i.e interfacial tension), circulator water bath was used to maintain the temperature constant. The surface tension measurement was carried out at 30°C, using circulator water bath.

#### **3.2.2.2 Plate Method.**

In the plate method, surface tension can only be measured and there are no measurements in push or pull direction. IFT cannot be measured with this method . Essentially the procedure is the same as in the ring method. However, in this case the plate was dipped into the liquid 2 mm deep before measurement started and lifted up to the level of the liquid surface. Most of the surface tension measurements were performed by the plate method at 30°C.

## CHAPTER 4

### CYCLOPOLYMERS OF DIALLYL QUATERNARY AMMONIUM SALTS: SYNTHESIS AND SOLUTION PROPERTIES.

#### 4.1 INTRODUCTION.

Since the discovery that radical polymerization of diallyl quaternary ammonium salts yields water-soluble cyclopolymers instead of cross-linked polymers [87–91], homo- and co-cyclopolymers of various diallylamine compounds have been extensively studied and their synthesis, kinetics, ring-sizes, properties and applications have been reviewed [84–86,92]. Cyclopolymerization and cyclocopolymerization of the diallylammonium compounds produce mostly ring structures. In a series of studies of the radical-initiated polymerization of unsaturated ammonium salts, Negi et. al [74], reported that diallyl quaternary ammonium salts polymerized in the presence of catalytic quantities of tert-butylhydroperoxide (T-BHP) or ammonium persulfate (APS) to form water-soluble polymers. In their studies, water and dimethylsulfoxide (DMSO) were used as solvents and found that free diallylamines do not polymerize, but their protonated and quaternary ammonium salts polymerized by radical initiation.

Quaternary ammonium chlorides polymerize more easily to give polymers having higher molecular weight than quaternary ammonium bromides [74]. Degree of polymerization (DP) of 5-100 has been estimated for allyl compounds polymers and their viscosity behaviours have also been studied [74]. The viscosity of these polymers is low when compared to what is usually required in most enhanced oil recovery applications. Although allyl compounds have been

reported to yield polymers of low molecular weight because of degradative chain transfer [74].

Complete or partial substitution of longer alkyl chains (hydrophobic groups) on to the backbone of these polymers would be expected to change the properties of the polymers such as viscosity, solubility and interfacial tension behaviours. Furthermore, because the cyclopolymers possess hydrophilic protonated or quaternary ammonium groups (polyelectrolyte polymer) and with their hydrophobic long alkyl chains, the polymers may form polymeric micelles and polymeric aggregates or self-oriented polymeric systems [86]. As a result of the amphiphilic nature of these polymers, they are also expected to give low surface and interfacial tensions. In view of these expected dual behaviours of the polymers (i.e high viscosity and low interfacial tension), we became interested in synthesizing the polymer for application in enhanced oil recovery. Polymers can enhance viscosity if they form interchain association structures [25,26].

Butler et.al [86], detected polymeric micelles of 1  $\mu\text{m}$  size and polymeric aggregates formed by a quaternary ammonium salt polymer from optical micrograph, but detailed properties such as viscosity and interfacial tension behaviours of the polymer which could be attributed to the structures of the polymers have not been investigated, at least to our knowledge.

In this study, attempts were made to synthesize cyclopolymers and cyclocopolymers of diallyl quaternary ammonium chlorides and bromides from N-ethylcyclohexylamine, Piperidine, Bis-(2-ethylhexylamine), Octylamine, Dodecylamine, Benzoylamine, and piperizine with the objective of investigating their viscosity and interfacial tension behaviours. Unfortunately, we were not

successful in polymerizing most of the polymers, except two (i.e from piperidine and piperizine). It was actually due to the use of inappropriate initiators. One of the polymer obtained from piperizine was found insoluble in water. However, the viscosity behaviour and surface activity of one of the polymers found soluble in water were investigated. Generally the viscosity of the polymer investigated was found lower than what is needed in enhanced oil recovery applications. However, the surface tension of the polymer was found low, thus displays high surface active property, a behaviour that can be likened to that found in surfactant systems.

## **4.2 PREPARATION OF CYCLOPOLYMERS OF DIALLYL QUATERNARY AMMONIUM SALTS.**

### **4.2.1 Polymer Synthesis.**

#### **4.2.1.1 Preparation of Allylamines.**

The procedures of Negi et.al [74] and Harada et.al [78] were similarly applied in preparing allylamines from N-ethylcyclohexylamine, Piperidine, Bis-(-2-ethylhexylamine), Octylamine, Dodecylamine, Benzoylamine and Piperizine. As an example; 31.75 g (0.25 mol) of N-ethylcyclohexylamine was mixed with 21 g (0.25 mol) of sodium bicarbonate (  $\text{NaHCO}_3$  ) and sufficient amount of water was added until a paste solution formed. All these were mixed in a 500 ml three-necked flask, fitted with a reflux condenser, stoppers and a mechanical stirrer. 33.2 g (0.25\*1.1 mol) of allylbromide was then added dropwise, with continuous stirring for 15 minutes. After which, the stirring was continued and left in this condition for 23 hours. After which, the oily layer of

the reaction mixture was separated by washing with water, followed by sufficient amount of diethylether at the end of the reaction period. The oily layer was then collected in a 125 ml flask. The whole reaction process took place at ambient temperature. The thin layer chromatograph (TLC) of the reaction product was taken which confirmed the formation of the desired compound. The compound obtained was then fractionated under reduced pressure, b.p of 78–79° C (10 mbar). The NMR taken also confirmed the formation of the desired product. The weight of the compound was 23.62 g.

The same procedure was similarly applied in preparing allylamines from the other amines and obtained the desired compounds (preursors to monomers) for each cases. The product obtained for each of the cases include allylpiperidine from piperidine, N-ethylhexylallylamine from N-ethylhexylamine, Bis-(-2-ethylhexylallyl amine) from Bis-(-2-ethylhexylamine), Octylallylamine from Octylamine, Dodecylallylamine from Dodecylamine, Decanoylallylpiperizine from piperizine, and Benzoylallylpiperizine from piperizine.



#### 4.2.1.2 Preparation of Diallyl Quaternary Ammonium Salts.

DiallylN-ethylcyclohexylammoniumchloride, Diallyldibenzoylammonium chloride, Diallylpiperidinium chloride, Diallylbenzoylpiperizinium chloride, Diallyldecanoylpiperizinium chloride and bromides of all these salts were prepared from allylchloride, allylbromide, benzoylbromide and N-ethylcyclohexylallylamine, Benzoylallylamine, allylpiperidine, Benzoylallylpiperizine and Decanoylallylpiperizine respectively using the procedures of Negi et.al [74] and Harada et.al [78]. As an example; 12.5 g (0.1 mol) of allylpiperidine was added to 20 ml of acetone and stirred with magnetic stirrer. 13.7 g (0.113 mol) of allylbromide was then added dropwise. After 5 minutes, a precipitate formation was observed. After which the reaction mixture was continuously stirred and left in this condition for 24 hours at room temperature. After this period, the precipitate formed was filtered and washed twice with acetone. The crystals obtained were then recrystallized from acetone-ethylether and absolute ethanol. Then dried in vacuo.

The same procedure was similarly applied to prepare the other salts from their respective allylamines, allylchloride, allylbromide and benzoylbromide and obtained for each cases white hygroscopic crystals.

#### 4.2.1.3 Polymerization and Copolymerization

Attempts were made to polymerize some of the quaternary ammonium salts obtained in the previous section, such as DiallylN-ethylhexylammonium chloride, Diallyldibenzoylammonium chloride, Diallylbenzoylpiperizinium chloride and Diallyldecanoylpiperizinium chloride using ammonium persulfate

and tert-butylhydroperoxide as the initiators, and dimethylsulfoxide (DMSO) and water as the solvents. Some of the salts were also copolymerized with sulfur dioxide (  $\text{SO}_2$  ) and with each other. The procedures of Negi et al [74] and Harada et.al [78] were similarly applied in the polymerization reactions.

One of the examples of the polymerization reaction is as follows: 2.4 g of diallylbenzoylpiperizinium chloride was mixed with 5.48 g of distilled DMSO and 25 mg of ammonium per sulfate (APS) was then added. Prior to the addition of APS,  $\text{N}_2$  gas was blown in to the reaction mixture to stop  $\text{O}_2$  free radicals degradation . After which the reaction mixture was stirred with magnetic stirrer and left at  $33^\circ\text{C}$  for 2 hours. After this period, some viscosification was observed in the reaction mixture. A thickened gum (no movement of liquid) was actually observed after 17 hours of the reaction. This was left in this condition for another 3 days. After which, the reaction mixture was precipitated into diethylether and washed twice with excess diethylether. Then dried in vacuo. White crystals were obtained.

2 g (5.0 wt%) of the dried polymer was dissolved in 18 ml of distilled water by stirring with magnetic stirrer. The polymer was found soluble in water after 30 minutes.

Similarly, 1.5 g of 1,1-diallyl-4-decanoylpiperizinium chloride was mixed with 2 ml of distilled DMSO and 14 mg APS was then added. Again  $\text{N}_2$  gas was blown into the reaction mixture . This was done prior to the addition of APS. After which, the reaction mixture was stirred and left at  $35^\circ\text{C}$  for an hour. After this period, a thick solution was observed. At about 3 hours of the

reaction time, the reaction mixture solidified. Hardened white solid mixture formed after 36 hours of the reaction time. This was then precipitated into ethanol and washed twice with excess ethanol

A small amount of the polymer obtained was dissolved in water, but found insoluble. It was however found soluble in methanol with very high viscosification ability.

Example of one of the copolymerization reactions is as follows: 1.2 g of diallylpiperidinium chloride was mixed with 1.84g of 1,1-diallyl-4-decanoylpiperizinium chloride in a flask containing 5.0ml of DMSO. 30 mg of APS was then added after evacuating air from the reaction mixture by blowing  $N_2$  gas into it. The reaction mixture was then stirred and left at 33–34° C. After 24 hours of the reaction time, a thickened with some solid solutions was observed. At this stage additional 15 mg APS was added and the reaction continued for another 2 days. After which the reaction product was precipitated into acetone/ethanol and washed twice with same at 0° C. White crystals were obtained. The polymer obtained was found soluble in water, with lot of foams (turbid).

The same procedure was similarly applied for copolymerization of diallylN-ethyl cyclohexylammonium chloride and sulfur dioxide,  $SO_2$ . 1.45 g of the salt was mixed with 10 ml of liquidified  $SO_2$ , at -150° C. 15 mg tert-butylhydroperoxide and acetone were added. The reaction mixture was left without stirring for 36 hours. After which no apparent reaction with  $SO_2$ , was observed. Then 5.0 ml of NaOH solution was added to the reaction mixture at

room temperature and again left for another 5 days. After this period, thick, colorless liquid formed. The reaction product was then precipitated into acetone. Then dried in vacuo. White crystals were obtained. The polymer was found soluble in water, but with little viscosification ability. The reaction schemes and structures for all these processes are given in figure 4.1.

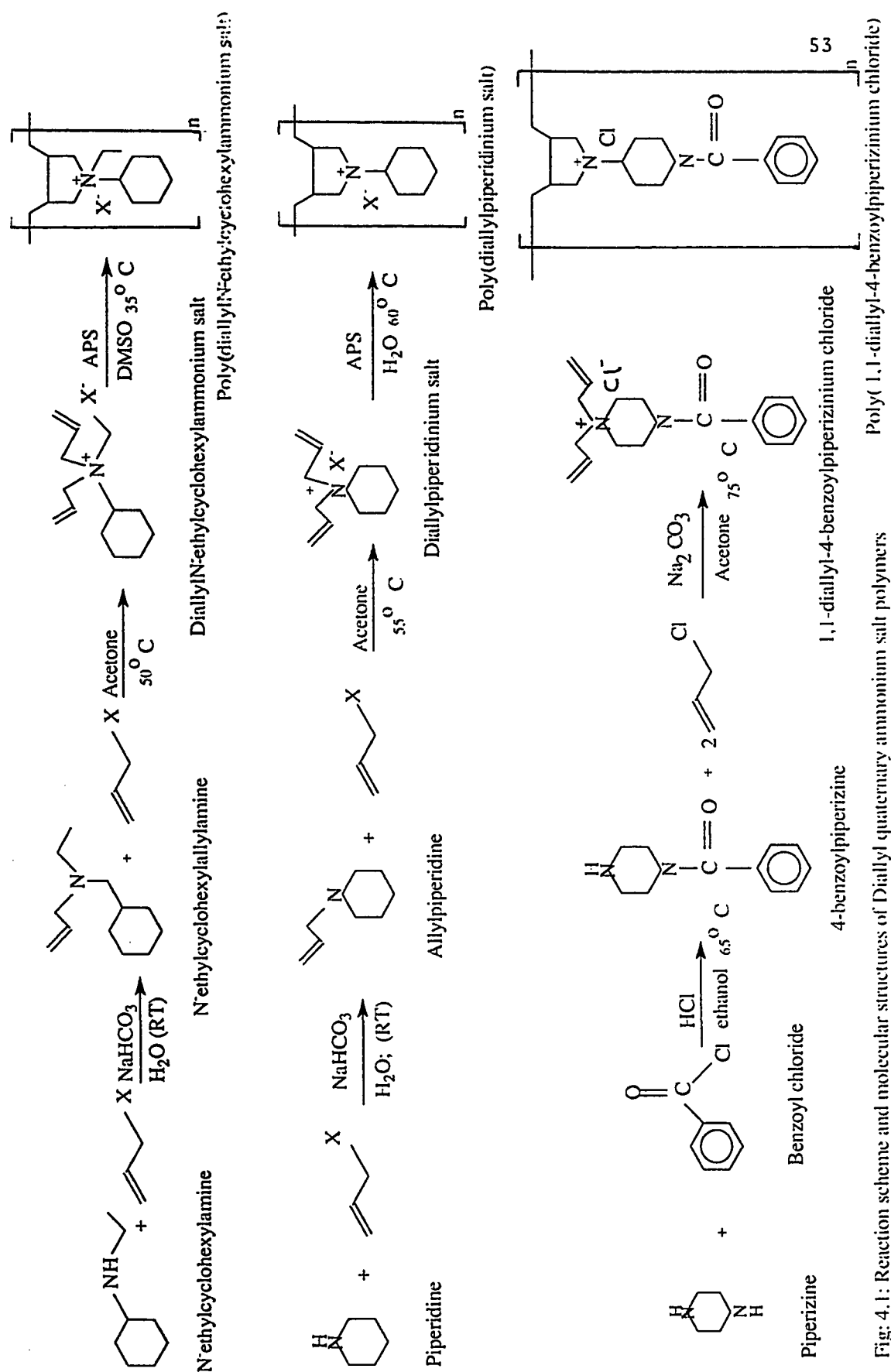


Fig. 4.1: Reaction scheme and molecular structures of Diallyl quaternary ammonium salt polymers

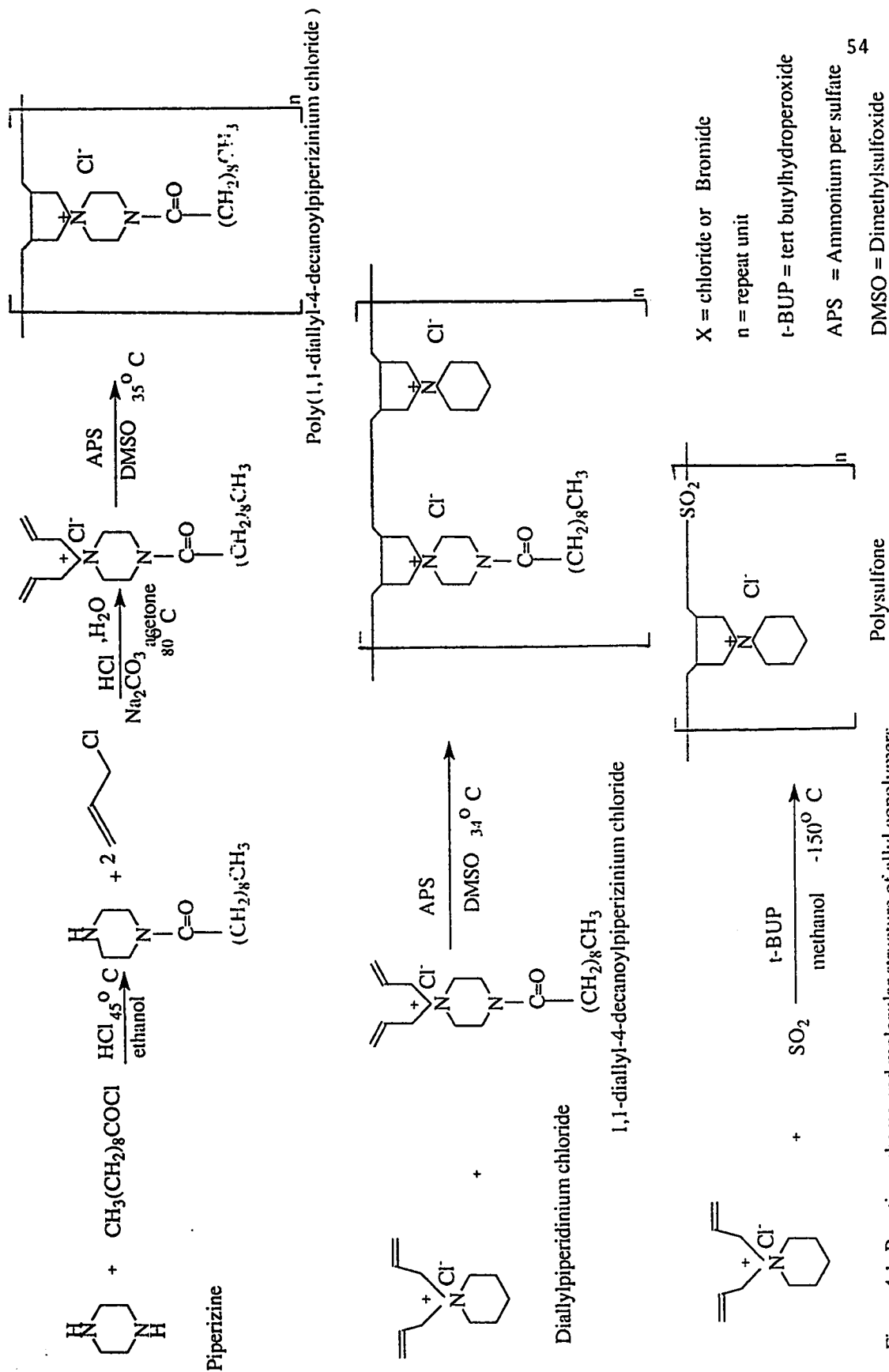


Figure 4.1: Reaction scheme and molecular structure of allyl copolymers

### 4.3 POLYMER CHARACTERIZATION.

#### 4.3.1 Elemental Analysis.

Elemental analysis to determine carbon, hydrogen and nitrogen content of some of the quaternary ammonium salt polymers obtained in this work was conducted at the central analytical laboratory of K.F.U.P.M research institute. The analytical data obtained are given in table 4.1

**Table 4.1: Elemental Analysis of Some of the Quaternary Ammonium salt polymers**

Polymer	%C	%H	%N
I	54.2	10.0	5.8
II	57.9	7.70	7.0

where

I = Poly(1,1-diallyl-4-decanoylpiperizinium chloride)

and

II = Poly(1,1-diallyl-4-benzoylpiperizinium chloride)

#### 4.4 POLYMER PROPERTIES.

The solution properties of the polymers such as viscosity behaviour and surface activity were not studied in detail because of their high NaCl salt intolerance. Most of the quaternary salt polymers obtained, precipitated in the presence of NaCl salt. However, the viscosity behaviour and surface activity of one of the polymers i.e 1,1-diallyl-4-benzoylpiperizinium chloride polymer that displays reasonable surface activity, but low viscosity were studied, with respect to polymer concentration, temperature and shear rate. The other polymers obtained from the synthesis were either found insoluble in water or displaying undesirable behaviour such as high sensitivity to salt and very low viscosity.

In this study, concentrated stock solutions were prepared under magnetic stirring at least 24 hours before use. Final solutions of desired composition were obtained by dilution of the appropriate stock solution with water and, if necessary, addition of appropriate amount of solid sodium chloride (NaCl). As an example; 2.0 g (10 wt%) of the 1,1-diallyl-4-benzoylpiperizinium chloride polymer crystals were dissolved in 18 ml of distilled water by stirring with magnetic stirrer for 30 minutes at ambient temperature. The polymer was found completely soluble at the end of this period. This was the stock solution. Subsequent compositions such as 5.0 wt%, 0.5 wt% e.t.c. were obtained by dilution of the appropriate amount of the stock solution.



#### 4.4.1 Viscosity Behaviour of the polymer.

The solution viscosity of poly(1,1-diallyl-4-benzoylpiperizinium chloride) was determined using a digital Brookfield viscometer with UL adaptor accessories at shear rate ranging from 0.4 to  $73.4 \text{ s}^{-1}$ . All the viscosities for the polymer concentration of 5.0 wt% were measured at temperatures in the range of 30–60° C. The detailed procedure of the viscosity measurements is given in chapter 3 . The result of the viscosity measurement obtained in this work is shown in table 4.2.

Table 4.2 and figures 4.2 and 4.3 depict the effects of shear rate, polymer concentration and temperature on the viscosity of the polymer. As shown in figure 4.2, an almost shear rate independent viscosity is observed at high shear rate (  $> 40 \text{ s}^{-1}$  ). However for lower shear rate values a typical shear thinning behaviour appears, for both polymer concentrations considered, (i.e 10 wt% and 5 wt%), and at temperature of 30° C. In the same figure, an increase in viscosity is observed as polymer concentration increases from 5.0 wt% to 10 wt%. Figure 4.3 also displays a decrease in viscosity with increasing temperature for shear rate of  $73.4 \text{ s}^{-1}$ , and polymer concentration of 5.0 wt%.

The shear thinning behaviour displayed in figure 4.1 at low shear rates could be attributed to the uncoiling and aligning of the polymer chains when exposed to shear flow.

As mentioned earlier in the introductory section, the viscosity of this polymer is characteristically low, up to high polymer concentration. The unusually low viscosity is attributed to the intramolecular aggregation of the

hydrophobic sidechains, keeping the hydrodynamic radius small. Similar trend was observed for polysoaps by Anton [100]. Although a slight increase in viscosity is observed with increasing polymer concentration of the polymer as already pointed out above, this could be attributed to the increase in the intramolecular aggregation of the hydrophobic sidechains, which probably increases slightly the hydrodynamic radius. The increase could not have been due to the intermolecular association of the hydrophobic sidechains, since intermolecular hydrophobic aggregation usually leads to a very high viscosity.

In order to assess the effect of temperature on the solution viscosity behaviour of the polymer, the Brookfield viscosity of 5.0 wt% of the polymer solution was measured at four different temperatures and at shear rate of  $73.4 \text{ s}^{-1}$ . The viscosity of the polymer decreases with increasing temperature as shown in figure 4.3.

**Table 4.2: The Viscosity-Shear rate-Temperature Data**  
**for Poly(1,1-diallyl-4-benzoylpiperizinium Chloride).**  
**Measured for polymer concentrations of 10 wt% and 5 wt%.**

Viscosity for Polymer conc. of 5.0 wt%					Viscosity for 10% conc.
Shear rate ( 1/sec )	Viscosity at 30 degree C ( cps )	Viscosity at 40 degree C ( cps )	viscosity at 50 degree C ( cps )	Viscosity at 60 degree C ( cps )	Viscosity at 30 degree C ( cps )
7.3	-	-	-	-	4.59
14.7	2.50	-	-	-	4.01
36.7	1.10	-	-	-	3.84
73.4	1.02	0.83	0.81	0.79	3.82

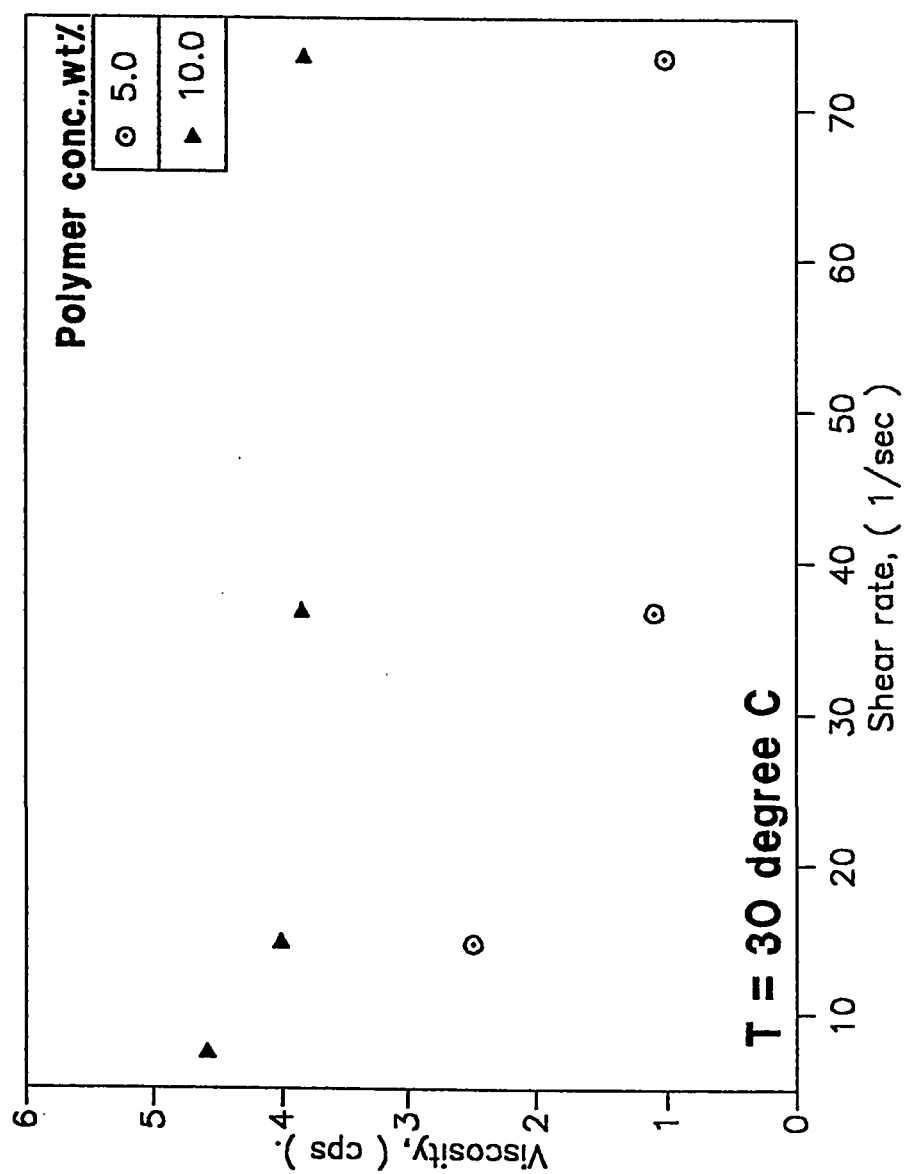


Figure 4.2 : Variations of viscosity—shear rate relationship with polymer conc. for Poly(1,1-diallyl-4-benzoylpiperizinium chloride)

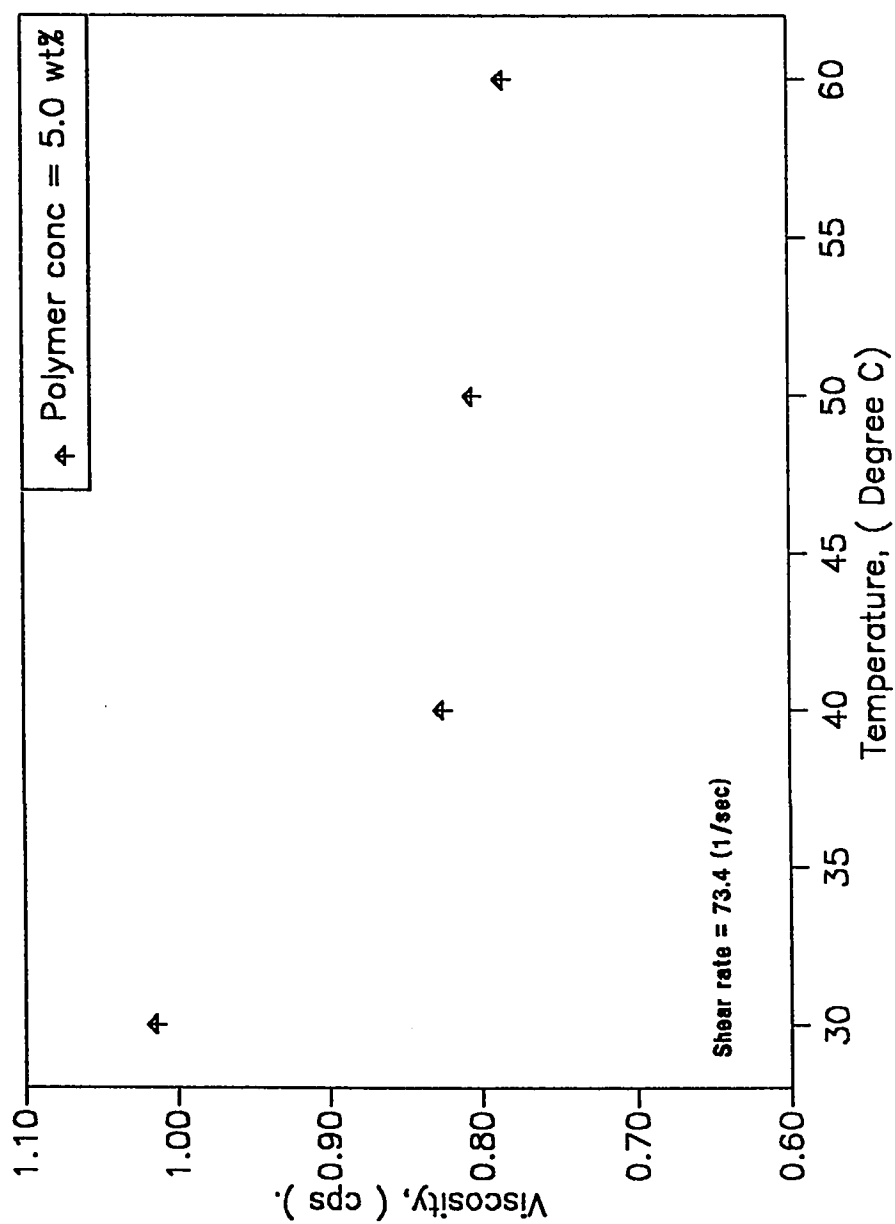


Figure 4.3 : Plot of viscosity versus temperature for Poly(1,1-diallyl-4-benzoylpiperizinium chloride) at polymer conc. of 5.0 wt%.

#### 4.4.2 Surface tension Behaviour of the Polymer.

The surface tension of the polymer was determined using a plate method. All the measurements for different polymer concentrations were determined at temperature of 30° C. The detailed description of the procedure of surface tension measurement is given in chapter 3 .

Table 4.3 and figures 4.4 and 4.5 show the effect of polymer concentration on the surface tension of the polymer of 1,1-diallyl-4-benzoylpiperizinium chloride. As displayed in the figures, a sharp decrease in surface tension with increasing polymer concentration is observed. This behaviour is expected for this polymer, because of its amphiphilic structure, a structure also possessed by surfactants. As the polymer concentration is increased, surface tension is lowered because of adsorption of the polymer molecules at the air-polymer solution surface. Actually the higher the concentration, the larger the adsorption (Adsorbed molecules are in equilibrium with bulk dissolved ones) and the lower the surface tension [83]. This phenomenon could be attributed to the amphiphilic structure of the polymers which probably causes concentration of the polymer molecules at the air-aqueous solution interface, thus causes reduction in the surface tension: [45]. Furthermore, No critical micelle concentration (CMC) or a break point resembling a CMC is observed for this polymer. This is in contrast to oligomeric polymer already studied [48]. More studies may be needed to obtain a full picture of the polymer surface tension behaviour.

**Table 4.3: The Surface tension-Polymer concentration Data for  
Poly(1,1-diallyl-4-benzoylpiperizinium Chloride),  
Measured at 30 degree C.**

Polymer conc. ( wt% )	Log Polymer conc. (wt%)	Surface tension ( mN/m )
0.10	-1.0	60.0
0.25	-0.602	48.74
0.50	-0.301	44.35
1.0	0.00	41.75
2.0	0.301	35.89
5.0	0.699	26.89
10.0	1.00	18.76

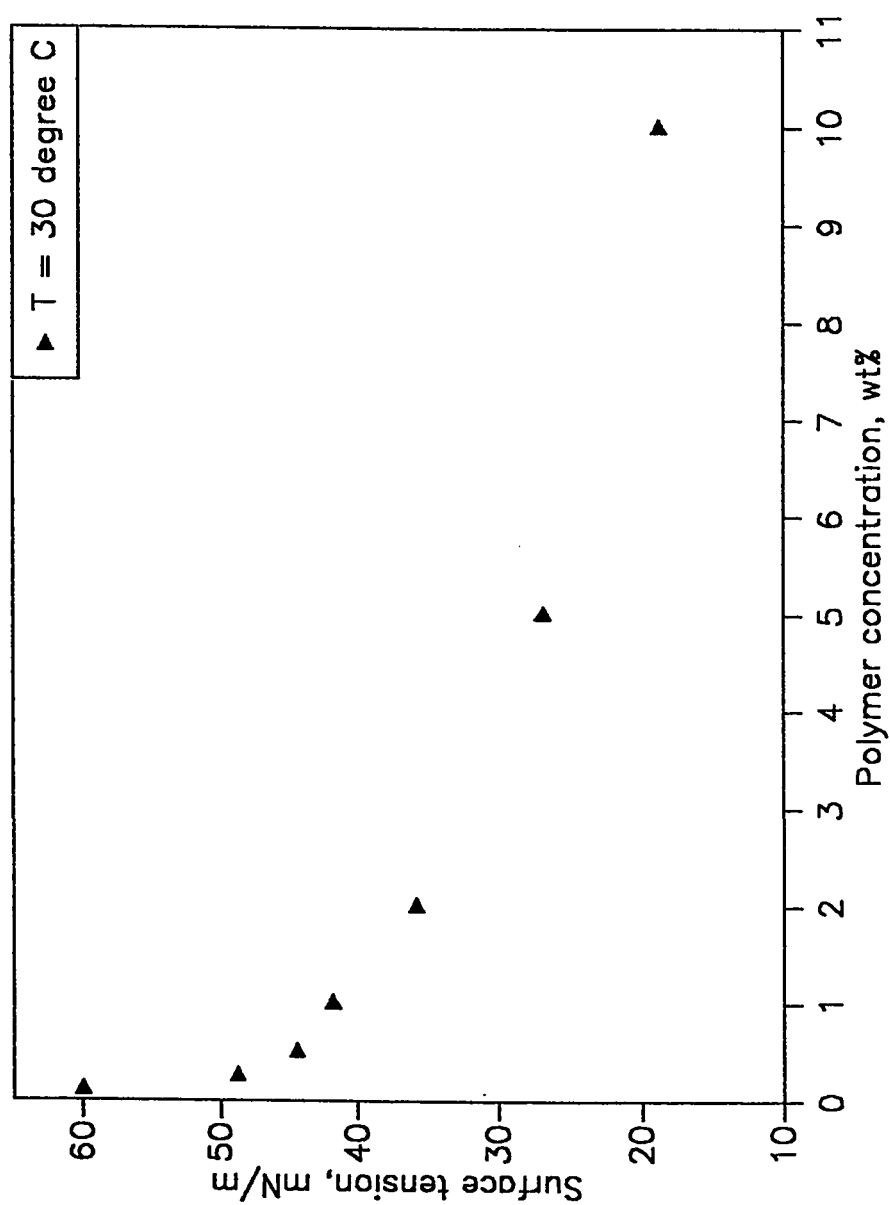


Figure 4.4 : Plot of surface tension versus polymer concentration ( wt% ) for Poly(1,1 -diallyl-4-benzoylpiperizinium chloride).



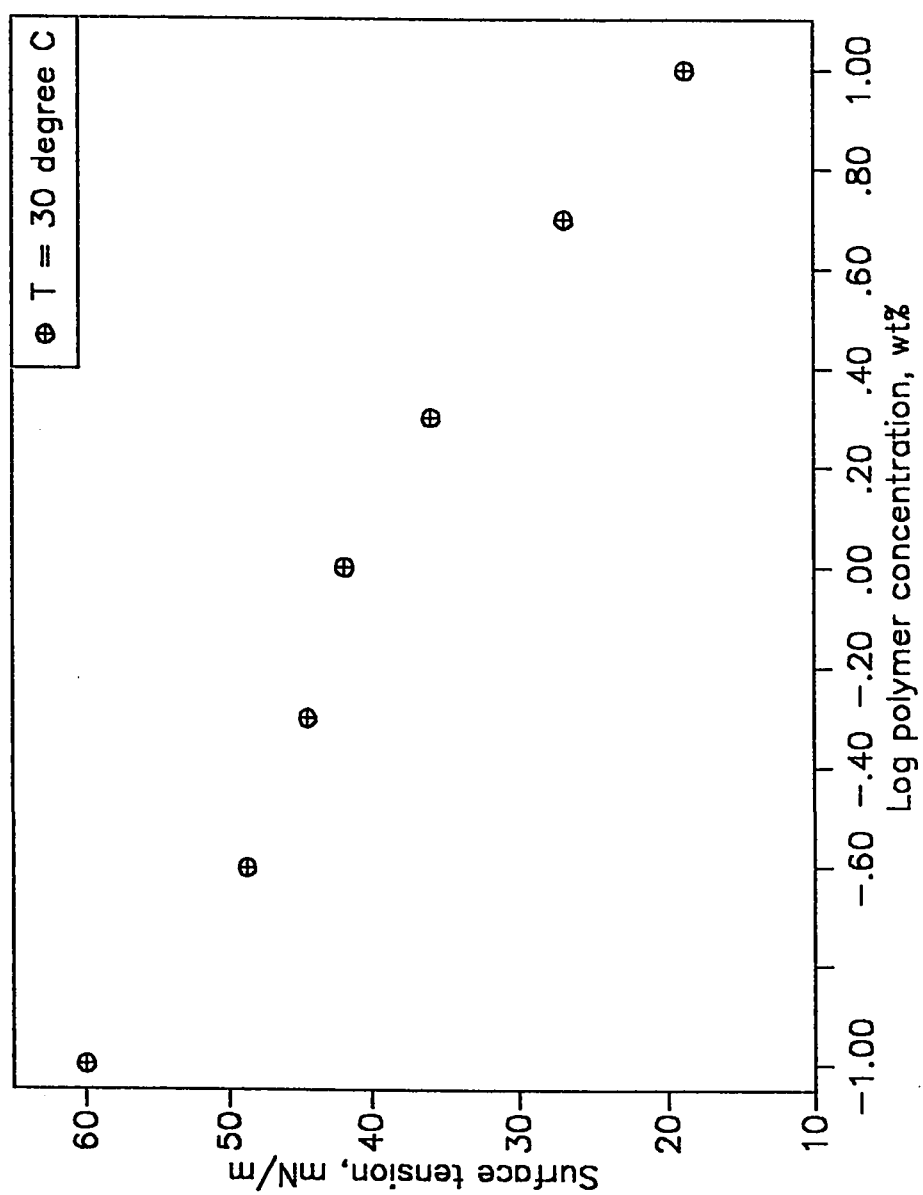


Figure 4.5 : Plot of surface tension versus log polymer concentration (wt%) for Poly ( 1,1-diallyl-4-benzoylpiperizinium chloride ).

#### 4.5 DISCUSSION AND CONCLUSIONS.

Generally, the viscosity of the polymer is low, even at high polymer concentrations. For this polymer, the hydrophobic interactions are predominantly intramolecular in nature, since intermolecular interactions would have resulted in a high rather than a low solution viscosity.

Furthermore, the polymer exhibits low salt tolerance. In as much as petroleum reservoir salinity can be very high, the polymer should be designed for high salt tolerancy. The high salt sensitivity exhibited by the polymer is probably due to its polyelectrolyte character.

The polymer also exhibits good surface activity that includes, low surface tension. The surface activity of this polymer could be compared to that of surfactant systems.

In general, the viscosity-shear rate relationship exhibits a nearly constant viscosity at high shear rate and a shear thinning behaviour at low shear rate. The shear thinning characteristics of this polymer would actually be an advantage in polymer flooding. Because, in the high shear region around the injection well bore, the effective viscosity of the injected polymer would be relatively low. Thus requiring low power to move. However, it would increase with decreasing shear as the polymer solution penetrates more deeply into the formation.

Increasing polymer concentration leads to an increase in polymer viscosity. Evidence of more intramolecular association of hydrophobic groups in the polymer is probably predominant as the polymer concentration increases. The

viscosity of the polymer decreases with increasing temperature. The surface tension also decreases with polymer concentration. Moreover, no CMC, or a break point resembling CMC is exhibited by the polymer.

## CHAPTER 5

### MALEIC ANHYDRIDE/1-ALKENE COPOLYMERS: SYNTHESIS AND AQUEOUS SOLUTION BEHAVIOURS.

#### 5.1 INTRODUCTION.

Since the discovery of the alternating copolymers of propylene with butadiene or isoprene, this copolymerization technique has been extended to reactions involving substituted olefins, substituted dienes, and substituted acetylenes [56–60]. A number of olefins, ethylene, cis-butene-2, trans-stilbene, allylacetate, undergo alternating copolymerization with maleic anhydride. The reaction with ethylene, under pressure, and in the presence of benzoyl peroxide, has been described in detail [56] and this procedure was also applied to propylene, 1-dodecene, vinylacetate, methylether, and styrene [56,57]. Alternating copolymers involving substituted maleic anhydrides and alkenes have been reported as well [58–60].

These polymers have also been studied from a different perspective. The micellization of a series of alternating comb-shaped copolymers, poly(1-alkene-co-maleic anhydride), in the diacid state in water with 1-alkenes ranging from 1-octene to 1-octadecene and weight-average molecular weights from 6000 to 20,000 have been studied using small-angle neutron scattering (SANS) technique. [93–94]. It was found that the copolymer derived from 1-octadecene forms cylindrical-shaped micelles, while the copolymers derived from lower 1-alkenes form ellipsoidal-shaped micelles with the transition occurring at the 1-hexadecene copolymer. The formation of micelles by copolymers of maleic

anhydride/1-alkenes with hydrophilic ester and ether groups ( $\text{CH}_2 - \text{CH}_2\text{O}$ ), and hydrophobic alkyl sidechains, ( $\text{CH}_3(\text{CH}_2)_n$ ), and ionic carboxyl groups has also been studied. A microscopic model for the formation of micelles by the polymers has been developed [95,96]. It has also been reported that alternating structures are likely to be obtained through the copolymerization of electron-donor-type monomers with electron-acceptor-type monomers. A system which produces a 1:1 structure is generally evidenced by a maximum in the rate of polymerization and/or degree of polymerization at an equimolar ratio, and this in itself has been cited as indicative of an alternating product [97]. Furthermore, as a result of amphiphilic structure of these polymers, a structure which can be likened to that of surfactants, the polymers are expected to show good surface and interfacial activities. In view of these expected behaviours of the polymers, we became interested in synthesizing the polymer for utilization in enhanced oil recovery.

A number of U.S. patents has reported the synthesis and viscosity behaviour of maleic anhydride/1-alkenes terpolymers. In one of the patents [61], the copolymers of maleic anhydride with long 1-alkene sidechain ( $> \text{C}_{30}$  and  $\text{C}_{18}\text{-C}_{20}$ ) have been found to be waxy materials, but have high viscosity, while copolymers of maleic anhydride with short alpha olefin chain (i.e  $\text{C}_6\text{-C}_{10}$ ) have been found to have low viscosity, but without the waxy character. Alternating copolymers of maleic anhydride have also been reported to exhibit low surface tension [62]. Most especially effective are maleic anhydride (acid and/or salt) copolymers with a relatively hydrophobic comonomer such as an alkyl vinyl ether. Hamad et.al [49], has also established the ability of amphiphilic sidechain

polymers to reduce the surface tension in a study of the solution behaviour of a comb-like commercial polymer Dapral GE-202.

In contrast to the large number of studies of the polymerization of alternating copolymers and formation of micelles by these polymers, investigations with the aim of establishing the general solution properties such as viscosity and interfacial activity behaviours are somewhat fewer. Although some investigations on the viscosity behaviour and surface activities of these polymers have been carried out, detailed solution properties, most especially interfacial tension behaviour of the polymer that could be attributed to the polymer structures have not been investigated atleast to our knowledge.

In this work, synthesis of copolymers of maleic anhydride with 1-dodecene and 1-hexadecene were carried out with the aim of investigating their viscosity and interfacial tension behaviours. From the study, the viscosity of the hydrolyzed polymers investigated was found to be low. The low viscosity obtained is probably due to the promotion of less intermolecular hydrophobic associations and more intramolecular interactions leading to collapse of the polymer into a random coil, thus reduces hydrodynamic volume of the polymer structure and consequently causes reduction in the viscosity. Furthermore, the polymers considered in this study are of low molecular weight. However, the polymers were found to exhibit good surface and interfacial activities. The surface and interfacial tensions of the polymers were found to be low. Their activities could be likened to surfactant like structures.

## 5.2 PREPARATION OF COPOLYMERS OF MALEIC ANHYDRIDE/1-ALKENE .

### 5.2.1 Polymer Synthesis.

The radical copolymerization reactions carried out in this work were performed in the experimental set-up shown in figure 3.1. Two 1-alkene, 1-dodecene and 1-hexadecene were copolymerized with maleic anhydride using benzoyl peroxide as the initiator. The copolymerization reactions were performed through radical initiation mechanisms. The procedures of Johnson et.al [56], and Braun et.al [57], were similarly applied in this work. As an example; 84.1 g (0.5 mol) of 1-dodecene (95% purity), 49 g (0.5 mol) of maleic anhydride (97% purity) and 0.05 g (0.2 mmol) of benzoyl peroxide were placed in a 500 ml three necked flask, fitted with stirrer, thermometer and reflux condenser. The reaction mixture was stirred at ambient temperature for 5 minutes. After which the reaction mixture was heated to 160° C in an oil bath and continuously stirred. Upon attainment of this temperature over a period of one hour, the reaction mixture was then held at 160° C for another 4 hours. After which, a clear homogeneous solution was obtained. The solution contents of the flask were then poured into a 250 ml flask to cool. A highly viscous waxy material was obtained at the end of the cooling process.

The same procedure was applied to copolymerize 1-hexadecene with maleic anhydride, except that, this reaction took 7 hours as against 4 hours taken by the copolymerization of 1-dodecene and maleic anhydride before a clear homogeneous solution is obtained. A highly viscous waxy material was also

obtained for this case.

### 5.2.2 Polymer Purification.

The highly viscous waxy materials obtained for both copolymers were purified by dissolving them in about 500 ml of tetrahydrofuran (THF) and co-precipitated into about 750 ml of methanol. The white precipitate obtained was allowed to settle and then filtered. The polymer obtained was then washed twice with excess amount of methanol, and dried in a vacuum at about 70° C. A white powdering polymer material was obtained at the end of the drying process.

### 5.2.3 Hydrolysis of the Copolymers

The two copolymers obtained were hydrolyzed in sodium hydroxide (NaOH) solution by heating. As an example; 3.33 g of the purified copolymer of maleic anhydride/1-dodecene was added to 50 ml (0.5M) of NaOH solution in a 100 ml round bottomed flask, fitted with a reflux condenser. The reaction mixture was then stirred and heated to boiling, ( 125° C ), for about 1 hour. After which, the reaction mixture was observed to be cleared. The hot contents were then poured into a glass bottle to cool.

Another example is as follow: 4.03 g of the purified copolymer of maleic anhydride/1-hexadecene was added to 50 ml (0.5M) of NaOH solution in a 100 ml round-bottomed flask, fitted with a reflux condenser. The reaction mixture was then stirred and heated to boiling for a period of 1 hour. After which, a clear homogeneous solution was obtained. The hot contents were then poured into a glass bottle to cool. The reaction scheme and molecular structures of the



copolymers are given in figure 5.1

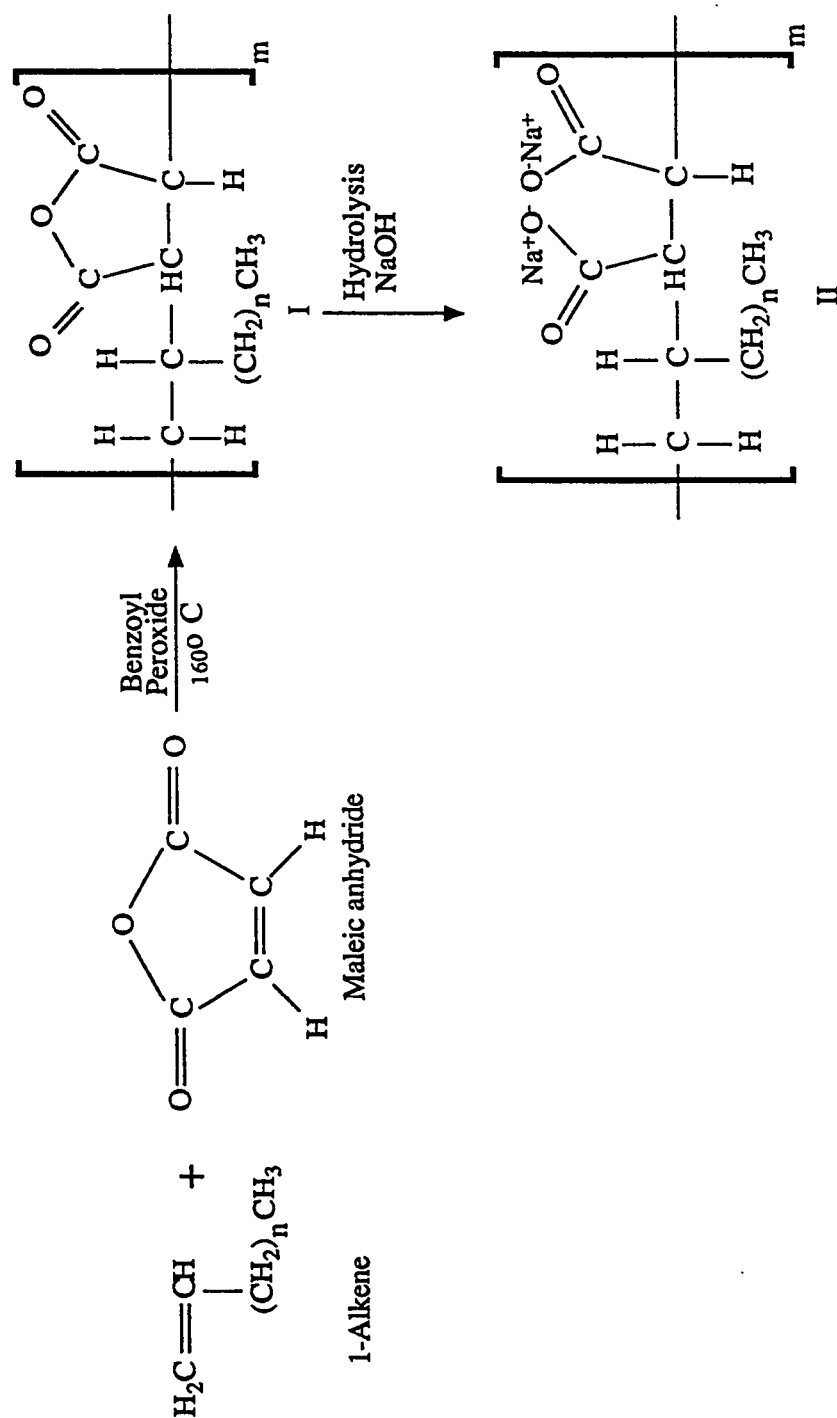


Figure 5.1: Reaction Scheme and Molecular structure of Copolymer of maleic anhydride/1-alkene

### 5.3 POLYMER CHARACTERIZATION.

#### 5.3.1 Elemental Analysis.

Elemental analysis to determine carbon, hydrogen and nitrogen content of the copolymers was conducted at the central analytical laboratory ( CAL ) of K.F.U.P.M, research institute. The analytical data obtained are given in table 5.1

**Table 5.1: Elemental Analysis of the Copolymers of  
Maleic anhydride/1-alkene.**

Polymer	%C	%H	%N
I	67.6	8.90	ND*
II	71.0	10.0	ND*

where

I = Poly(1-dodecene-co-maleic anhydride)

and

II = Poly(1-hexadecene-co-maleic anhydride)

ND\* = Not present.

## 5.4 POLYMER PROPERTIES.

The solution properties of the copolymers such as viscosity behaviour and surface and interfacial tensions were investigated with respect to temperature, polymer concentration, salinity and shear rate. In this work, concentrated stock solutions were prepared atleast 24 hours before use. Final solutions of desired composition were obtained by dilution of the appropriate stock solution with water, or NaOH solution and, if needed, addition of solid NaCl .

### 5.4.1 Viscosity Behaviour of the Copolymers

Solution viscosities of the two copolymers were determined using a digital Brookfield viscometer with UL adapter accessories at shear rates ranging from 0.4 to  $73.4 \text{ s}^{-1}$ . All viscosities for the copolymer concentration of 2.7wt%, 6.7wt%, 3.2wt% and 8.1wt% were measured at temperatures in the range of 25 – 90° C. The measurements are depicted in tables 5.2-5.5.

Tables 5.2-5.5 and figures 5.2-5.5 display the effects of shear rate, polymer concentration and temperature on the viscosity of the copolymers of maleic anhydride/1-dodecene and maleic anhydride/1-hexadecene. For the two copolymers considered, an almost shear rate independent viscosity is observed when shear rate is high, i.e 36.7 and  $73.4 \text{ s}^{-1}$ , as depicted in figures 5.2 and 5.4. In figures 5.3 and 5.5, an increase in viscosity is observed as the polymer concentration increases from 2.7 to 6.7wt% and 3.2 to 8.1wt% for the copolymers of maleic anhydride/1-dodecene and maleic anhydride/1-hexadecene respectively. This behaviour is observed for the two copolymers at shear rate of  $73.4 \text{ s}^{-1}$ , and for all temperatures ranges, i.e 25 – 90° C, considered.

As mentioned earlier in the introductory section, the viscosity of these polymers is characteristically low, up to high polymer concentrations. The unusually low viscosities are attributed to the intramolecular aggregation of the hydrophobic sidechains, keeping the hydrodynamic radius small. Similar trend was observed for polysoaps by Anton [100]. Although a slight increase in viscosity is observed with increasing polymer concentration of the copolymers as already pointed out above, this could be attributed to the increase in the intramolecular aggregation of the hydrophobic sidechains, which probably increases slightly the hydrodynamic radius. The increase could not have been due to the intermolecular association of the hydrophobic sidechains, since intermolecular hydrophobic aggregation usually leads to a very high viscosity.

Furthermore, figures 5.2-5.5 display the effect of temperature on the solution viscosity of the copolymers. A decrease in viscosity with increasing temperature is observed for the copolymers and for all the ranges of shear rate and polymer concentrations considered.

In order to assess the effect of NaCl on the solution viscosity of the copolymers, the viscosity of 2.7wt% of the polymer solution with NaCl salt concentration ranging from 0.1 to 1.0wt% was measured at 30° C. and at shear rate of  $73.4 \text{ s}^{-1}$ , for both polymers. The copolymer of maleic anhydride/1-dodecene is observed to be more salt tolerant than the copolymer of maleic anhydride/1-hexadecene. The former is tolerant to NaCl salt up to 1.0wt% NaCl salt concentration. After which, a precipitate formation was observed. However, the latter is observed to be tolerant up to 0.5wt% NaCl salt concentration. Beyond this concentration, a precipitate formed. The results of

the viscosity measurements with NaCl salt concentration and the effect of adding NaCl salt on the solution viscosity of the copolymers are displayed in table 5.6 and figures 5.6 and 5.7.

For the copolymer of maleic anhydride/1-dodecene, a salt tolerance behaviour is observed as depicted in figure 5.6 within the range of NaCl salt concentration considered. An increase in viscosity is observed up to 0.1wt% NaCl concentration and then levels off from 0.1wt% to 0.75wt% NaCl concentration. From 0.75wt%, a further increase in viscosity is observed up to the last point. However, an exponential increase is observed for the copolymer of maleic anhydride/1-hexadecene as the NaCl concentration increases. This behaviour is depicted in figure 5.7.

As expected for polyelectrolytes (charged polymers), addition of inorganic salts should bring about important changes to the behaviour of the polymers. The screening of charge repulsion tends to decrease the viscosity; and a drastic decrease of CMC resulting in a more effective interchain association. When viscosity enhancement due to interchain association prevails over polyelectrolyte effect, addition of NaCl salt results in an increase in viscosity of the polymer system. However, when interchain association in pure water is high enough, addition of salt leads to a more compact network which rapidly collapses [17,99]. Taking into account the above considerations, one can interpret the results of figures 5.6 and 5.7 in terms of hydrophobic chain aggregation. The increase in viscosity observed in both figures with increasing NaCl concentration could be attributed to the formation of large aggregates. In other words, the effective intramolecular association might have prevailed over polyelectrolyte

effect, thus addition of NaCl results in an increase in viscosity. As such the classical viscosity reduction of polyelectrolyte solutions in the presence of salts can be successfully prevented or reduced if the polyelectrolyte chain is grafted by a hydrophobic groups, as evidenced from the observation made with our copolymers and that of Wang et.al [17]. In these observations, hydrophobic groups aggregate all the more as ionic strength increases, leading to polymer chain association and thus to viscosity enhancement. All these observations suggest that effective hydrophobic association is favoured by the addition of salt. Similar observations have been reported for a polysoaps by Anton [100], and for associative acrylamide/N-alkylacrylamide copolymers by McCormick [4].

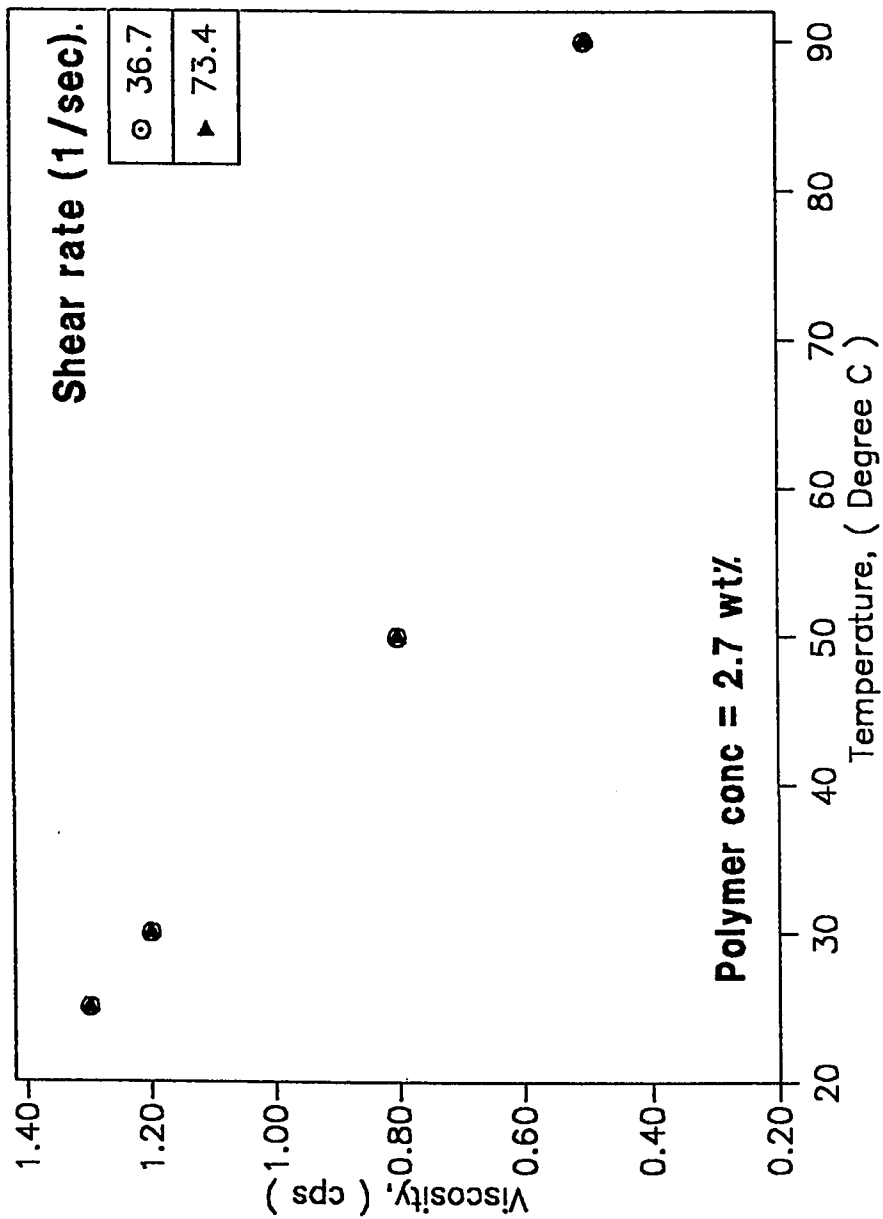


Figure 5.2 : Plots of viscosity versus temperature for the copolymer of maleic anhydride/1--dodecene for polymer conc. of 2.7 wt%.



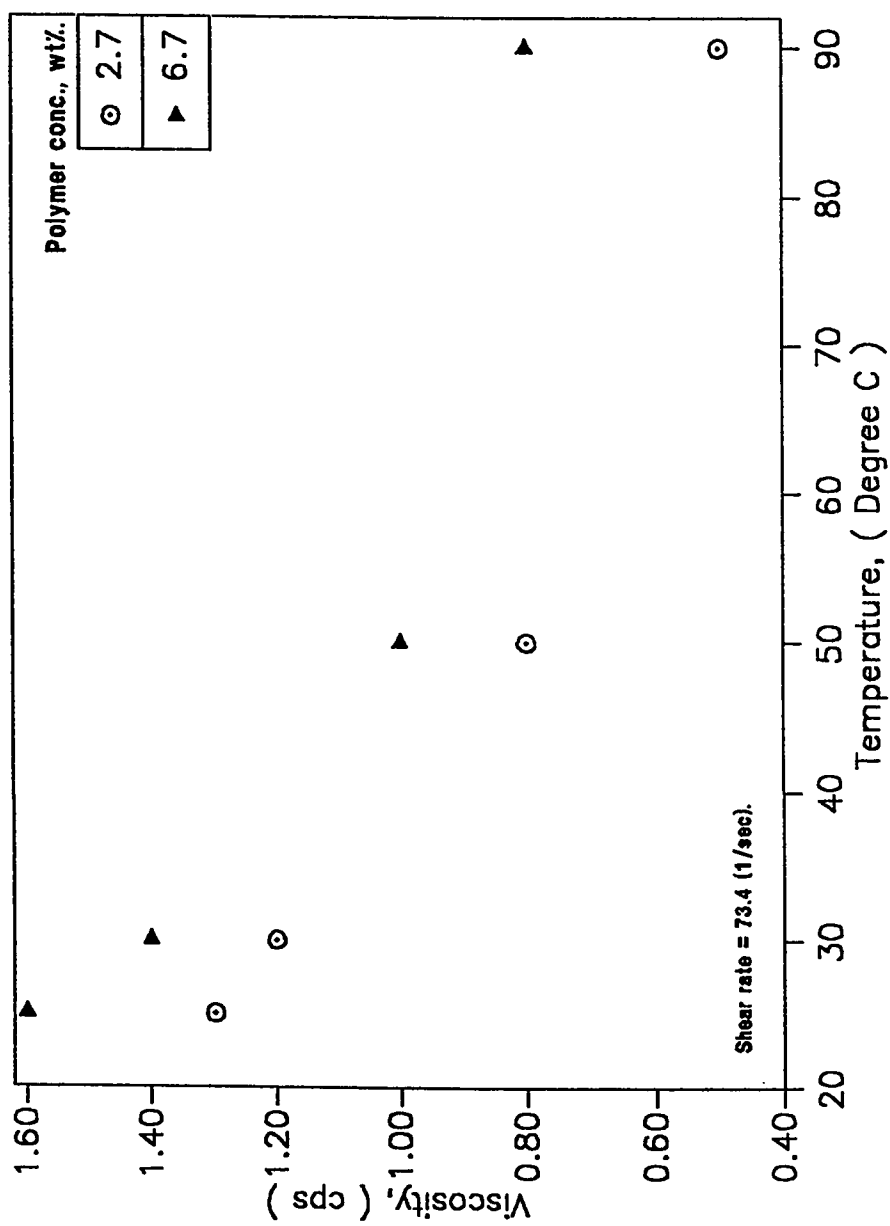


Figure 5.3 : Plots of viscosity versus temperature for the copolymer of maleic anhydride/1-dodecene at shear rate of 73.4(1/sec).

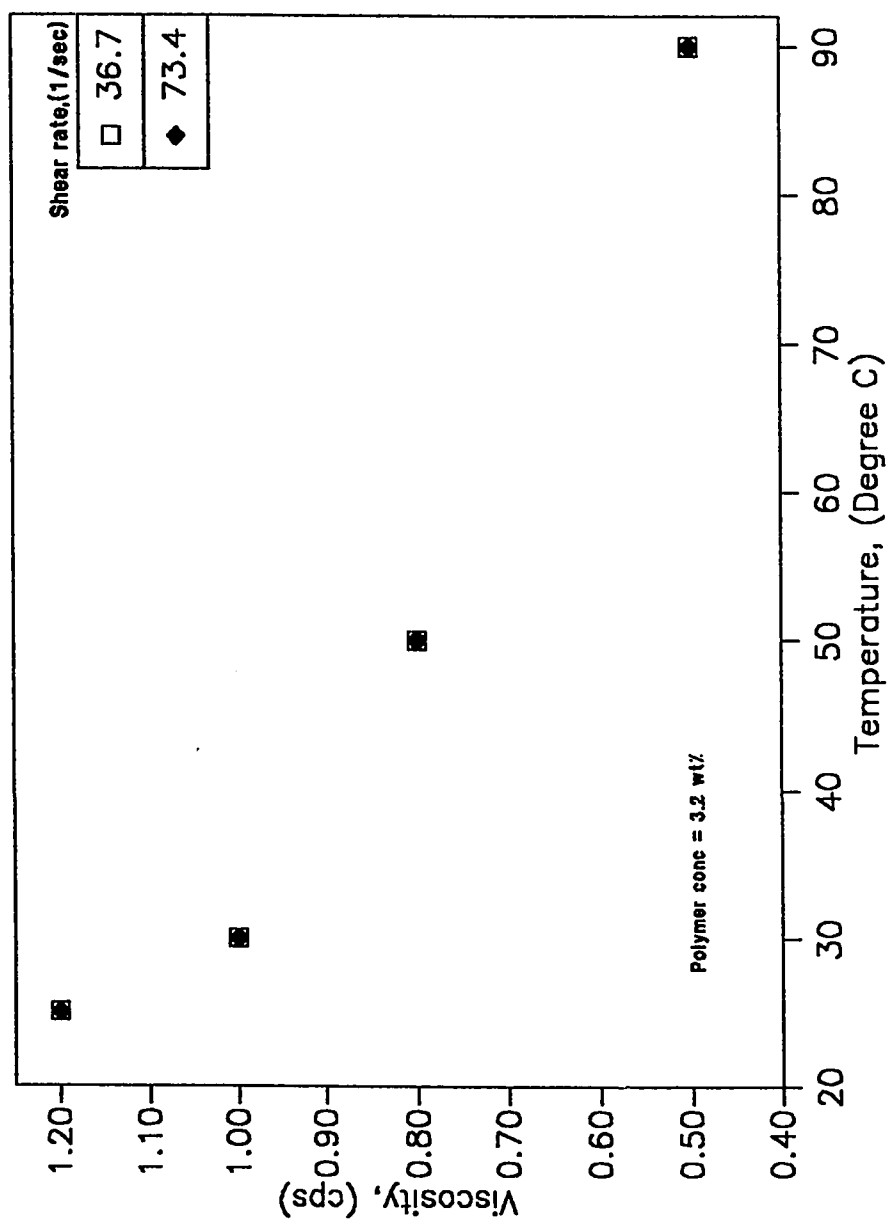


Figure 5.4 : Plots of viscosity versus temperature for the copolymer of maleic anhydride/1-hexadecene for polymer conc. of 3.2 wt%.

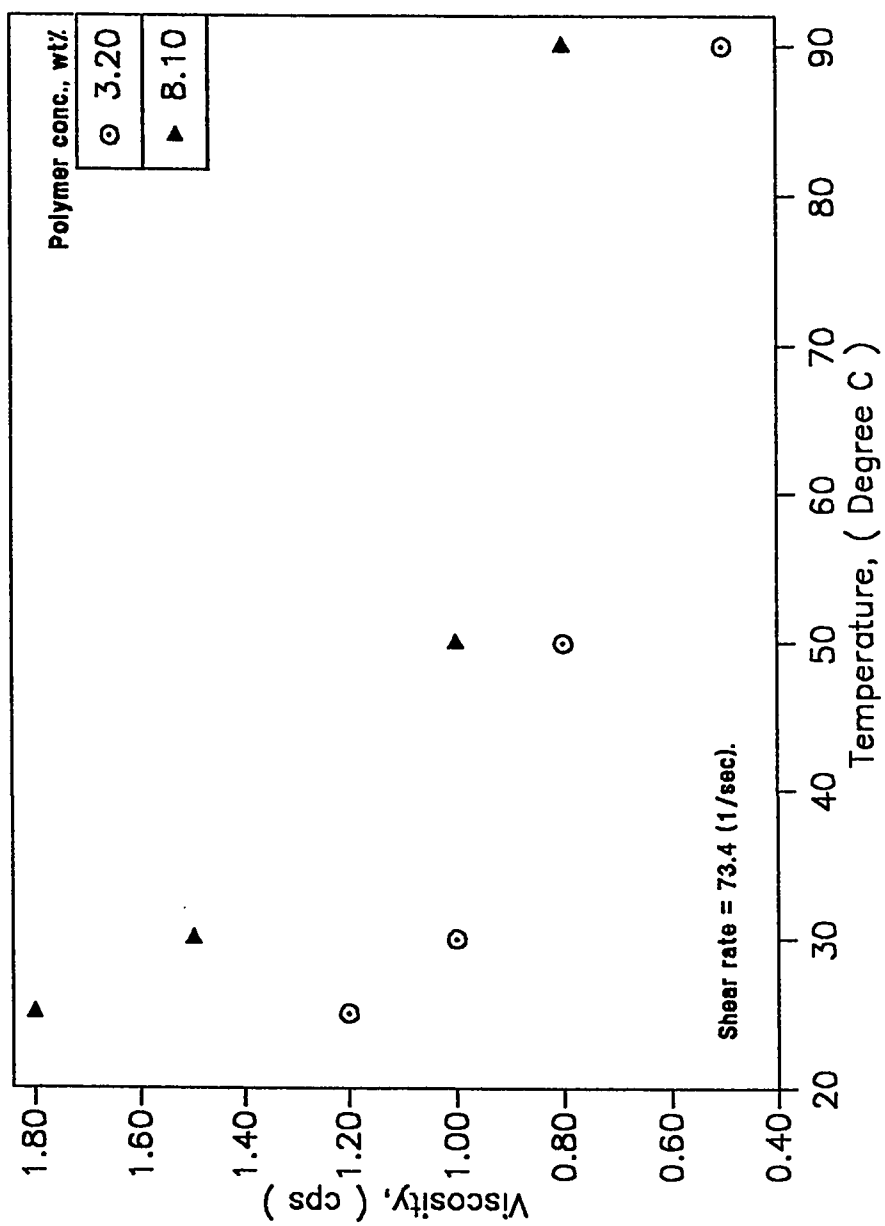


Figure 5.5 : Plots of viscosity versus temperature for the copolymer of maleic anhydride/1-hexadecene at shear rate of 73.4 (1/sec)

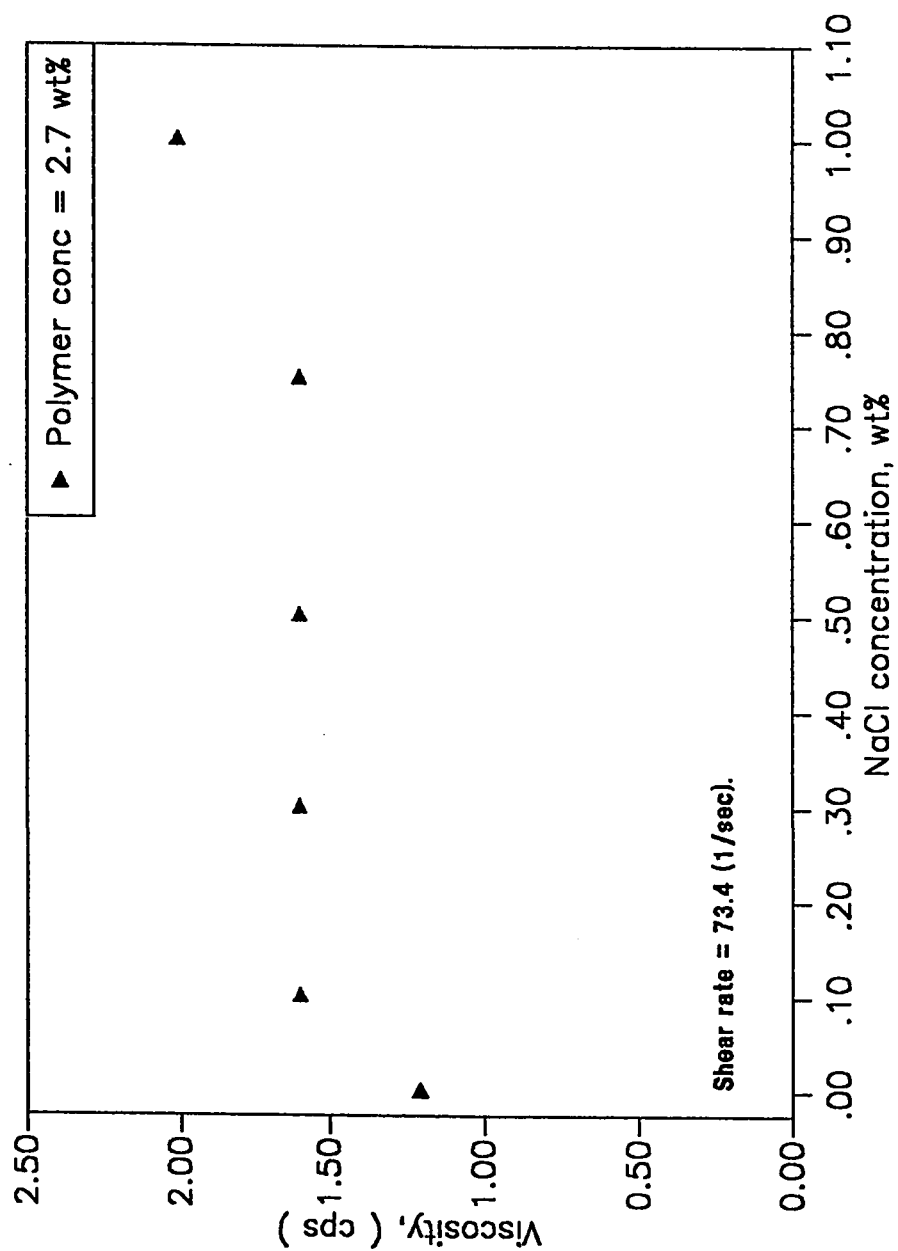


Figure 5.6 : Effect of NaCl concentration on the viscosity of copolymer of maleic anhydride/1-dodecene at 30 degrees C.

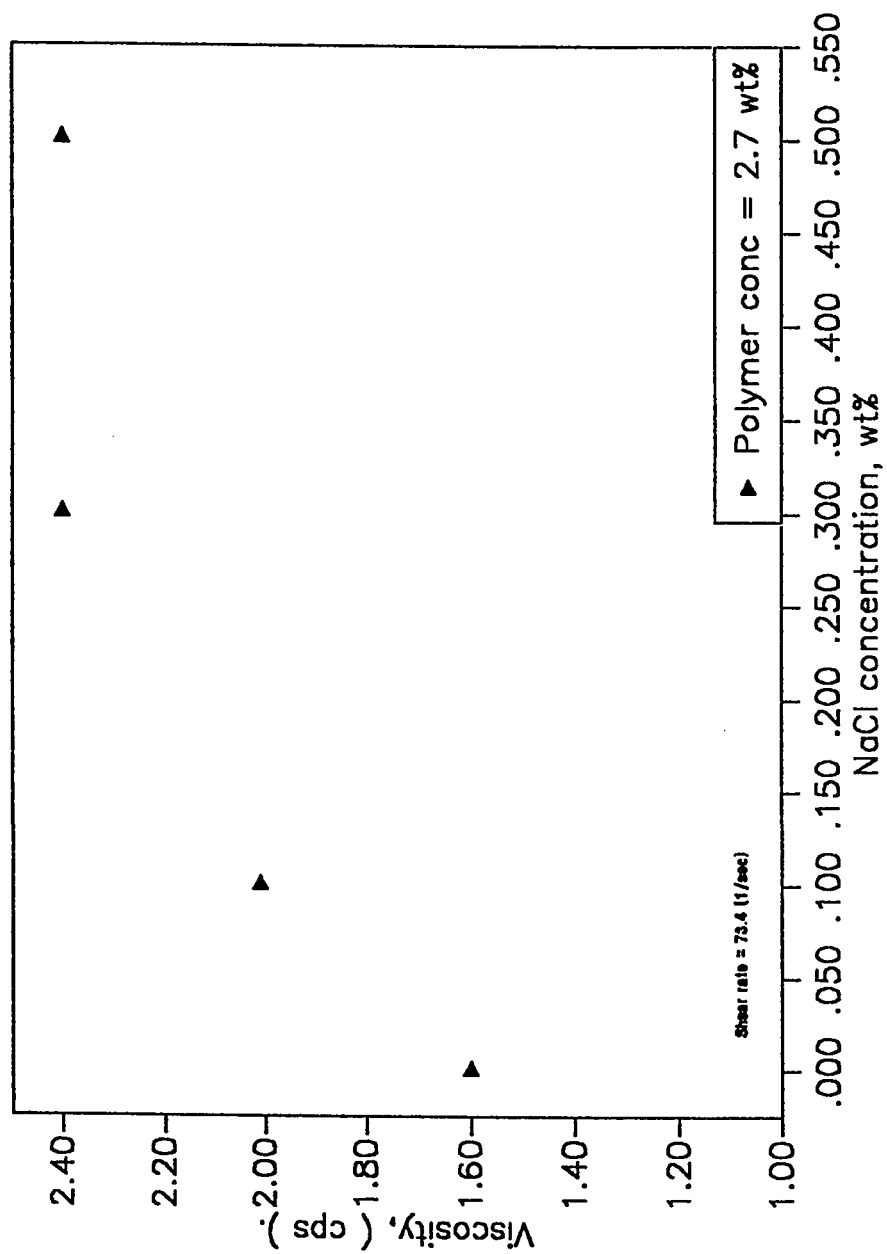


Figure 5.7 : Effect of NaCl concentration on the viscosity of copolymer of maleic anhydride/1-hexadecene at 30 degrees C.

#### 5.4.2 Surface tension Behaviour of the Copolymers.

The surface tensions of the copolymers were determined using the plate method. All measurements at different polymer concentrations were performed at 30° C. The detailed description of the procedure is given in chapter 3.

Tables 5.7-5.18 and figures 5.8-5.15 show the effects of polymer concentration and time on the surface tension of the two copolymers. As depicted in figures 5.8 and 5.9 for the copolymer of maleic anhydride/1-dodecene and figures 5.12 and 5.13 for the copolymer of maleic anhydride/1-hexadecene, a sharp decrease in surface tension is observed with increasing polymer concentration for both polymers. The surface tension decreases up to a well defined concentration, called critical micellar concentration, (CMC). Above this concentration, the tension remains nearly constant. The break point which resembles a CMC is observed to occur at the polymer concentration of 0.29wt% and the corresponding surface tension of 45 mN/m for the copolymer of maleic anhydride/1-dodecene . For the copolymer of maleic anhydride/1-hexadecene , the break point concentration observed is 0.491 wt% and the corresponding surface tension is 42.7 mN/m. As the polymer concentration increases, the surface tension decreases because of adsorption of more polymer molecules at the air-aqueous solution interface [83]. The increase in adsorption is attributed to the amphiphilic structure of the polymers which causes higher concentration of the polymers molecules at the air-aqueous solution interface and consequently causes reduction in the surface tension [45].

The time dependence of surface tension of the polymers are displayed in

figures 5.10 and 5.11 for the copolymer of maleic anhydride/1-dodecene and that of maleic anhydride/1-hexadecene is displayed in figures 5.14 and 5.15. The surface tensions of the copolymers decrease with time for polymer concentration of between 0.63 -2.50wt%. Below polymer concentration of 0.63wt%, a weak time dependence is observed.

The time-dependence could be attributed to the surface reorientation process of hydrophobic moieties or additional adsorption from the bulk phase to the air-aqueous solution interface. Extensive equilibration times are also required due to slow diffusion and conformational changes of the polymers [100]. Similar trends have also been observed by Okubo [37], and Ishimuro et.al [51,52].

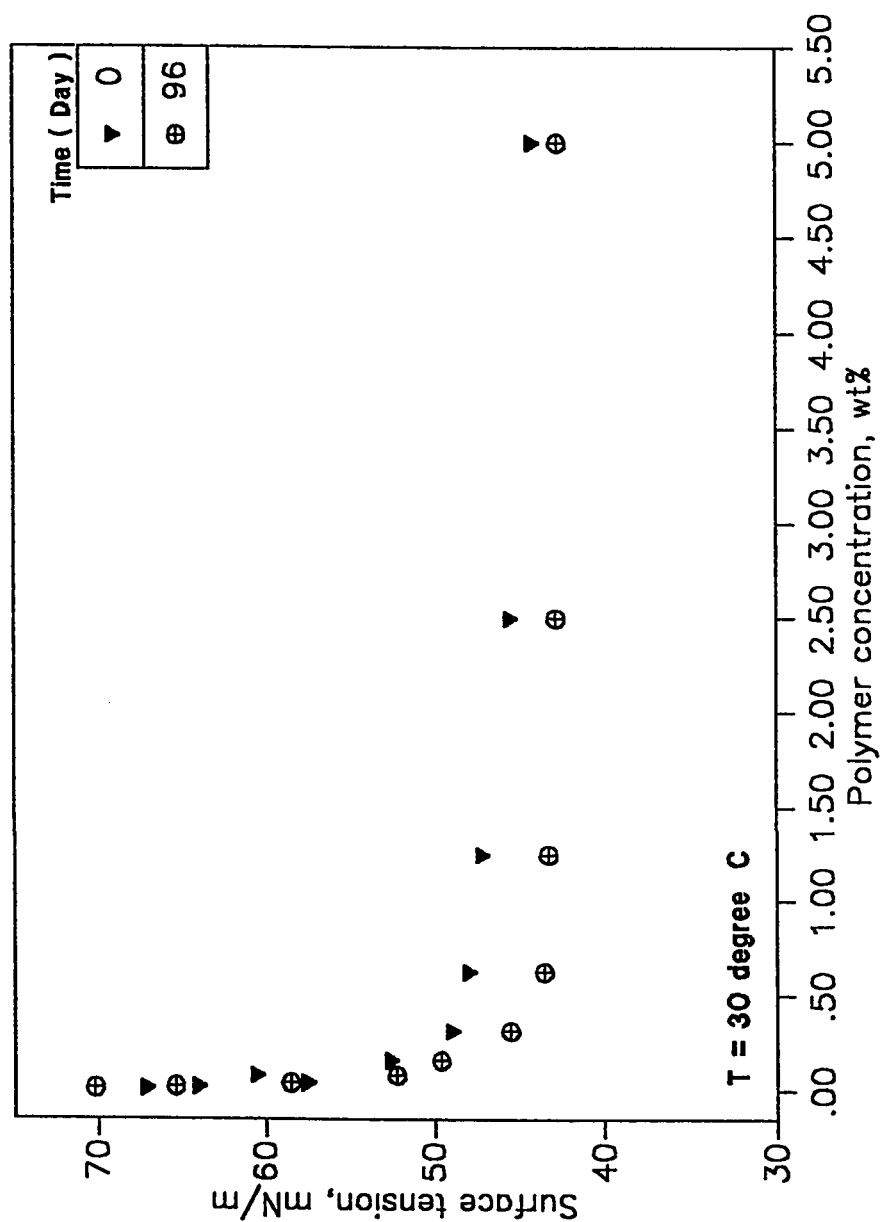


Figure 5.8 : Plots of surface tension versus polymer concentration ( wt% ) for the copolymer of maleic anhydride/1-dodecene.



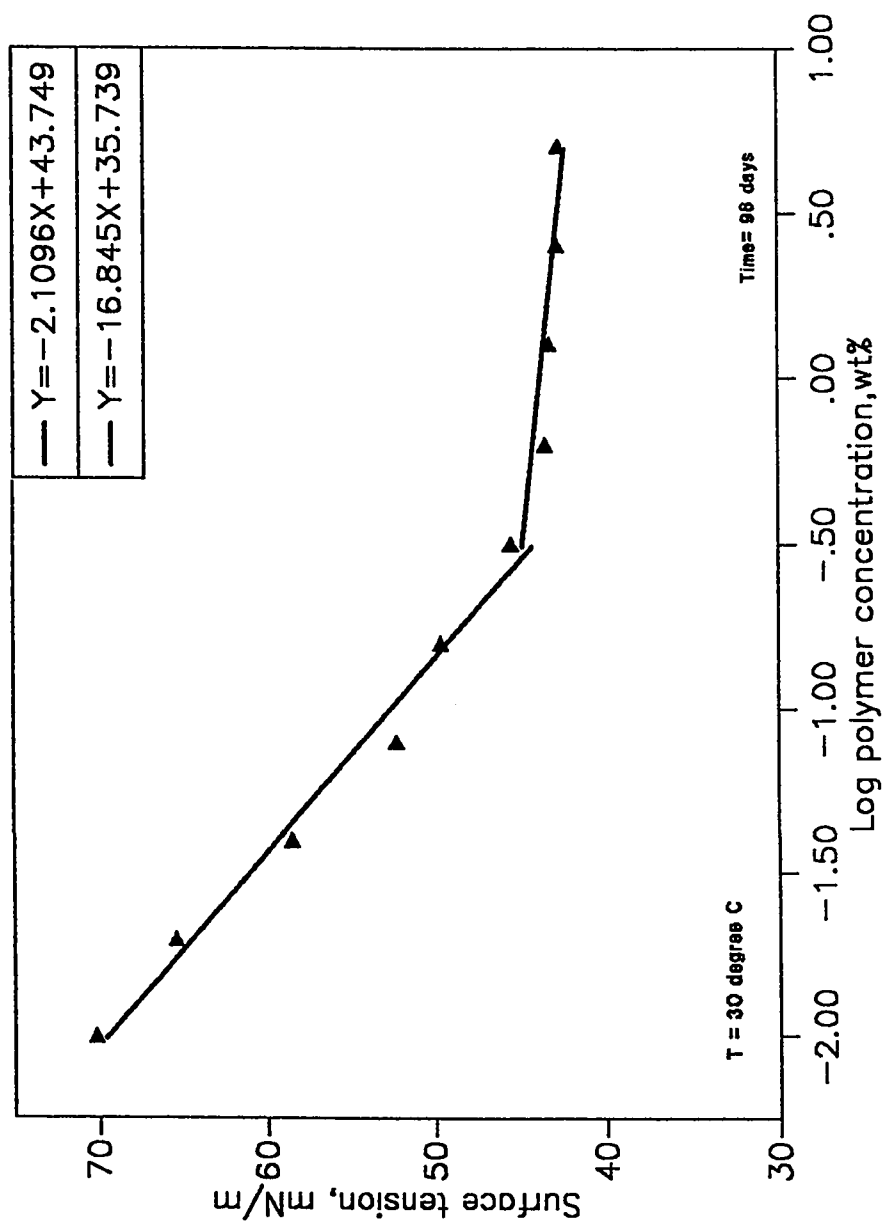


Figure 5.9 : Plots of surface tension versus log polymer (wt% ) concentration for the copolymer of maleic anhydride/1-dodecene.

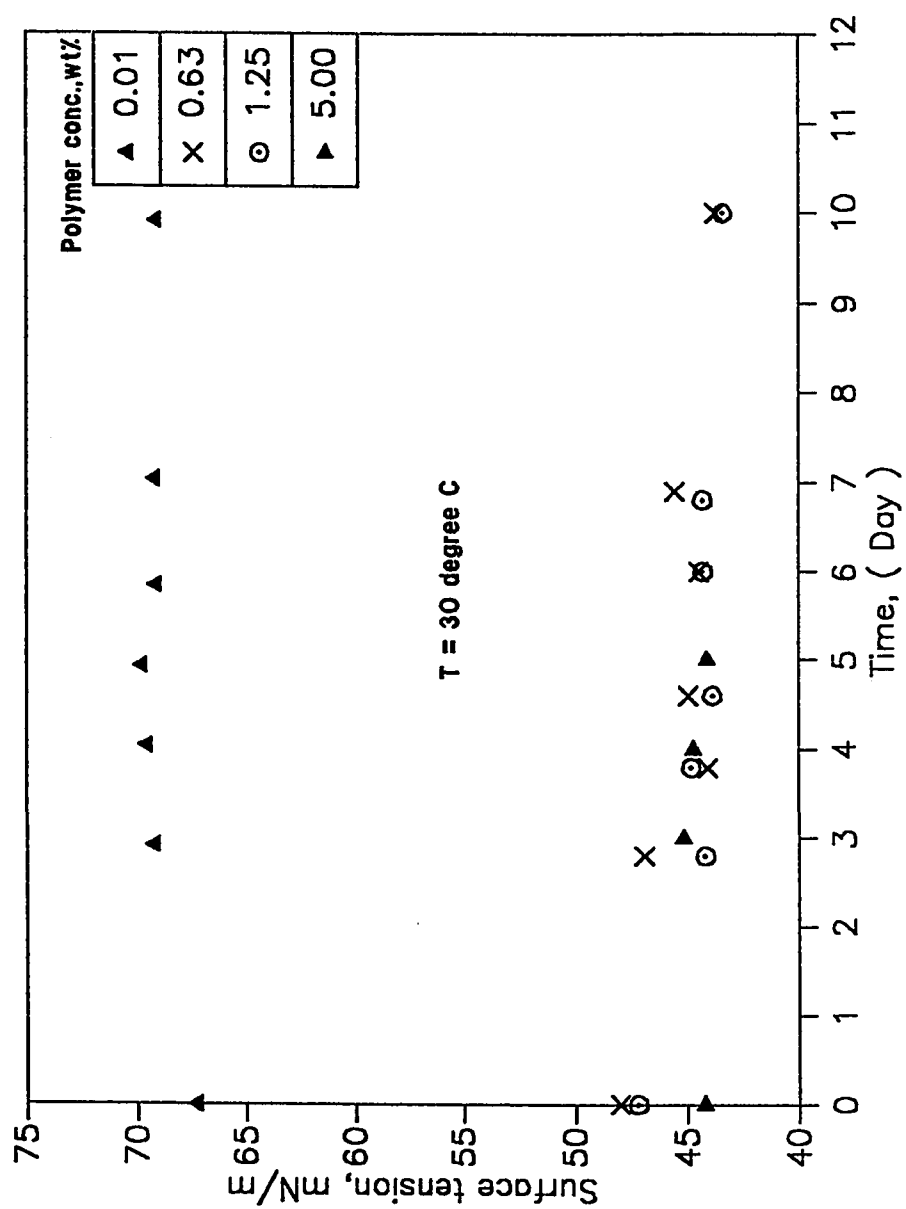


Figure 5.10 : Variations of surface tension—time relationship with polymer conc. for copolymer of maleic anhydride/1—dodecene.

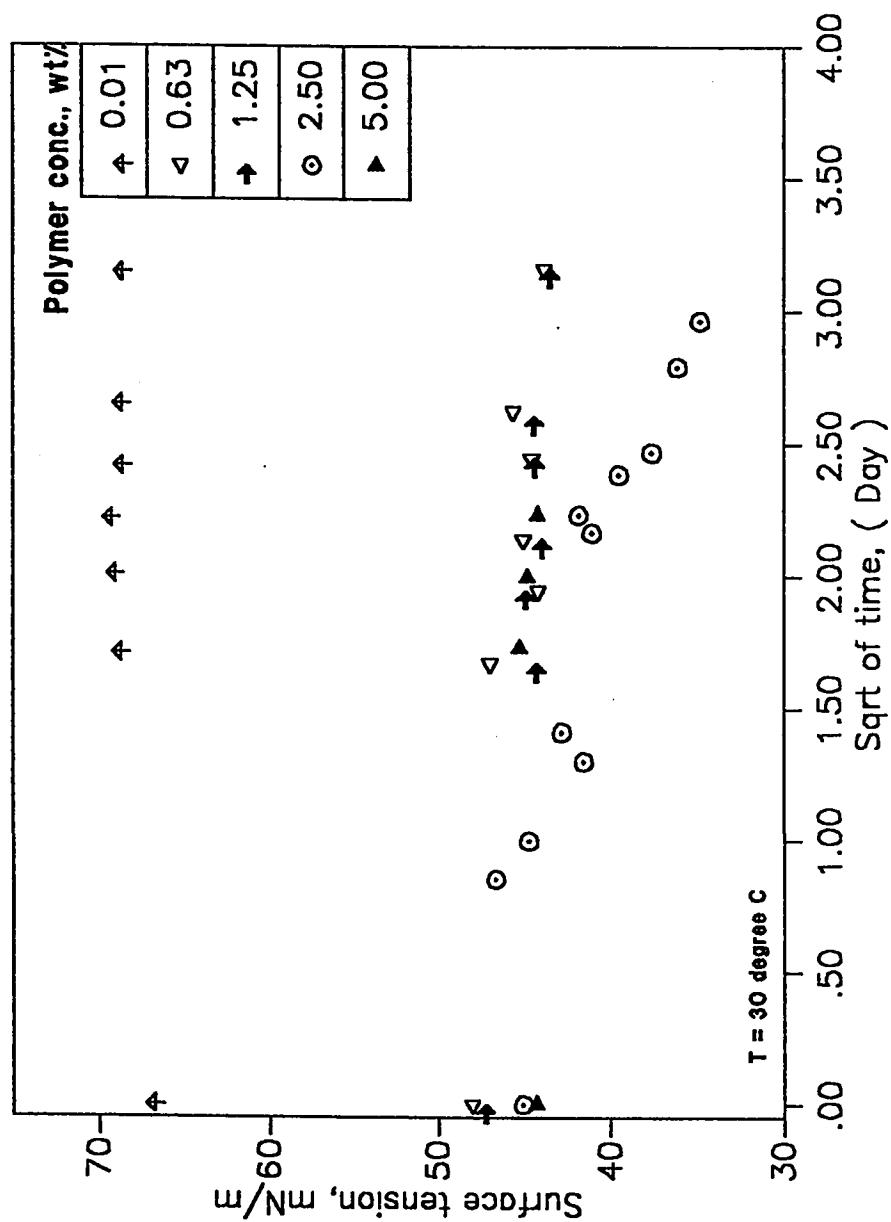


Figure 5.11 : Variation of surface tension—sqrt of time relationship with polymer conc. for copolymer of maleic anhydride/1—dodecene

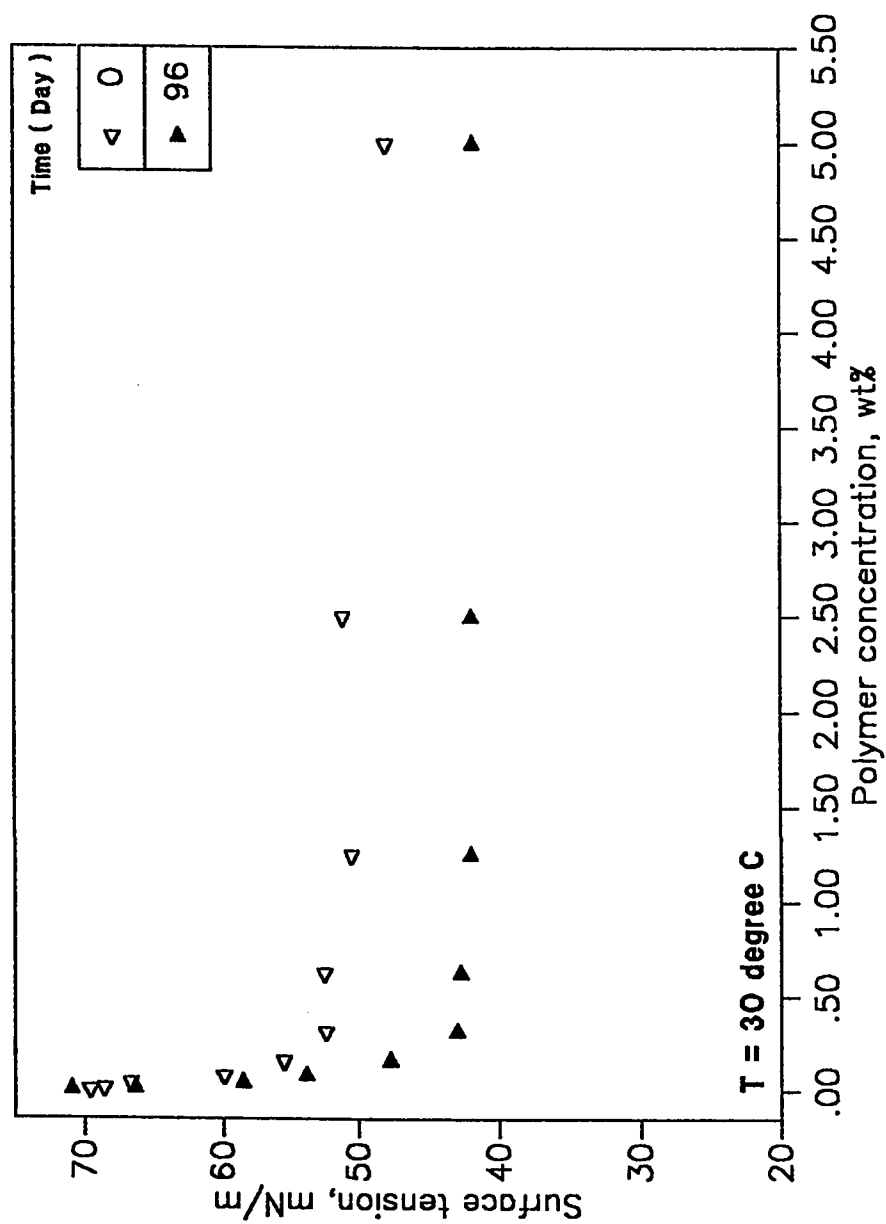


Figure 5.12 : Plots of surface tension versus polymer (wt%) concentration for the copolymer of maleic anhydride/1-hexadecene.

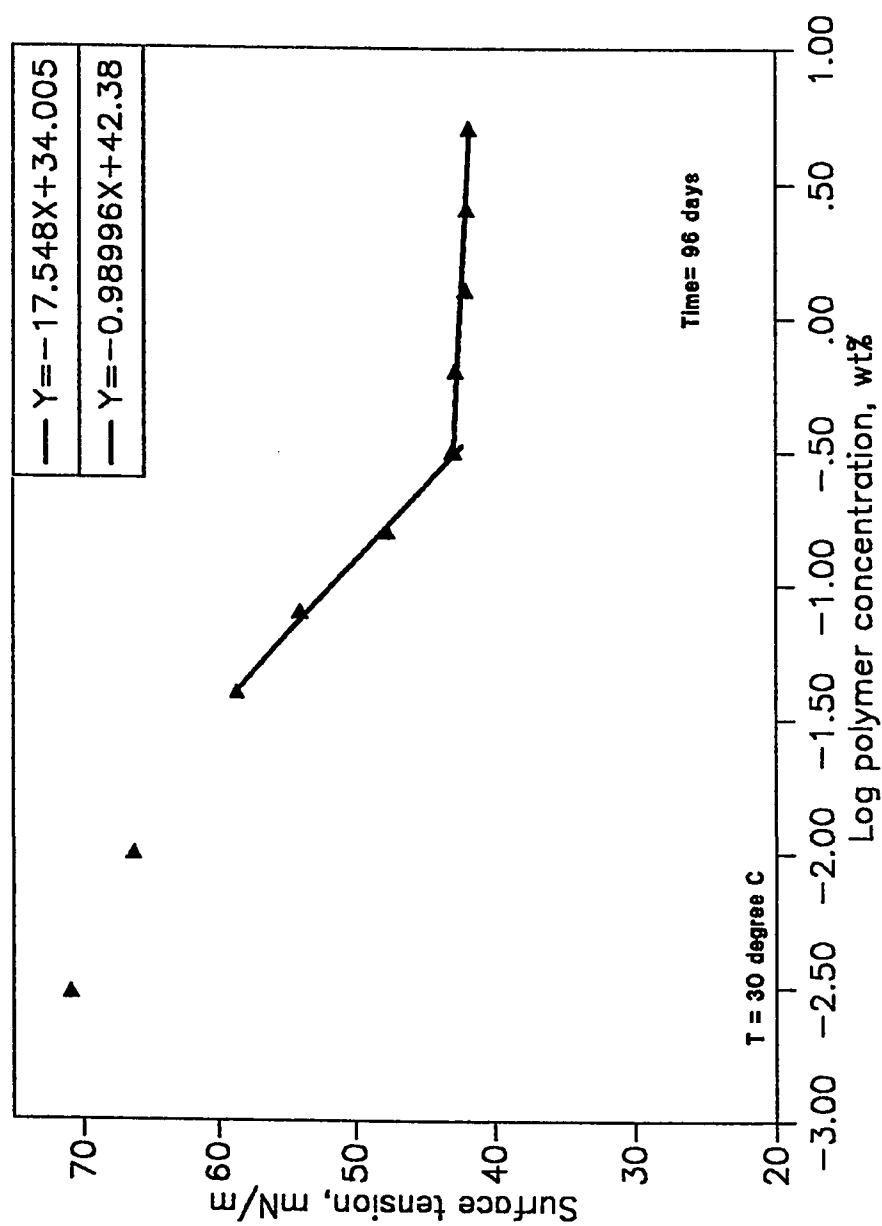


Figure 5.13 : Plots of surface tension versus log polymer (wt%) concentration for the copolymer of maleic anhydride/1-hexadecene.

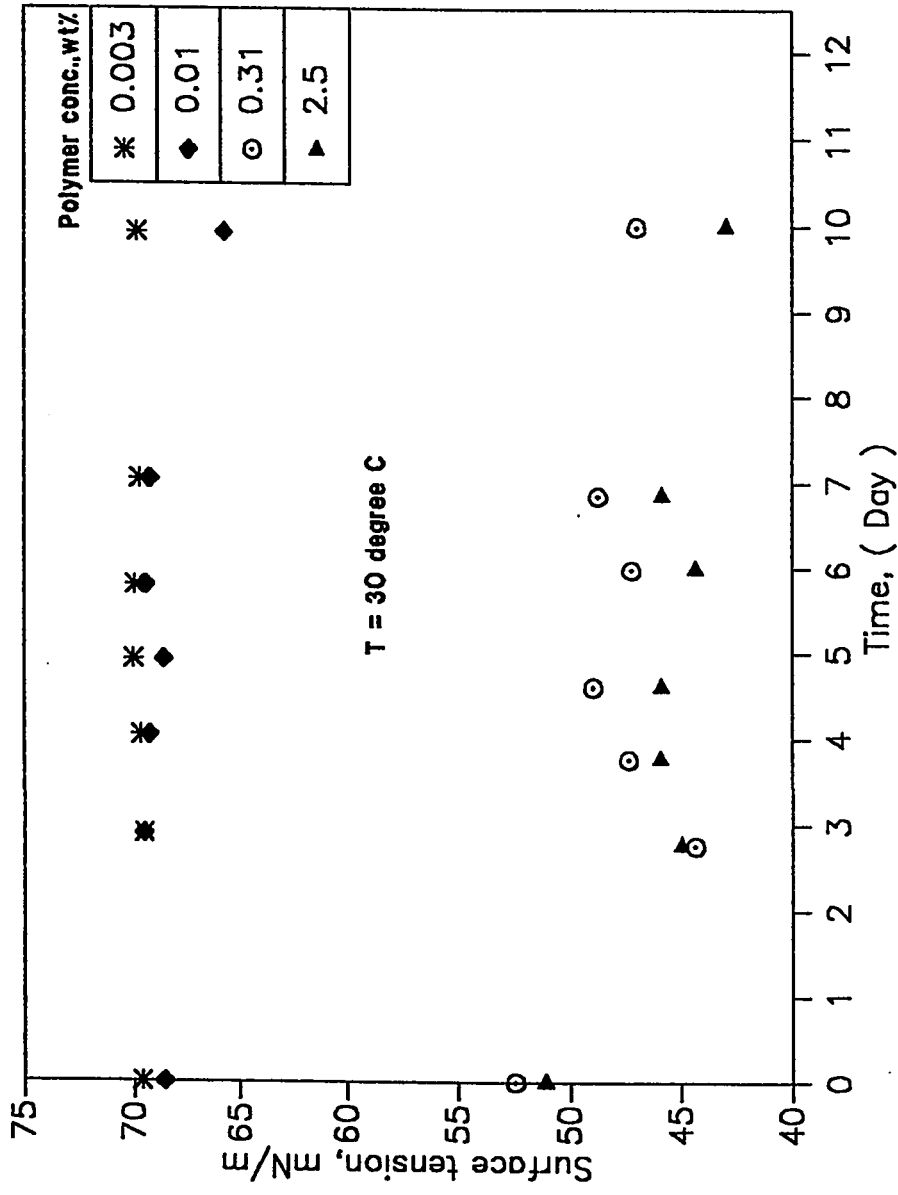


Figure 5.14 : Variations of surface tension—time relationship with polymer conc. for the copolymer of maleic anhydride/1—hexadecene.

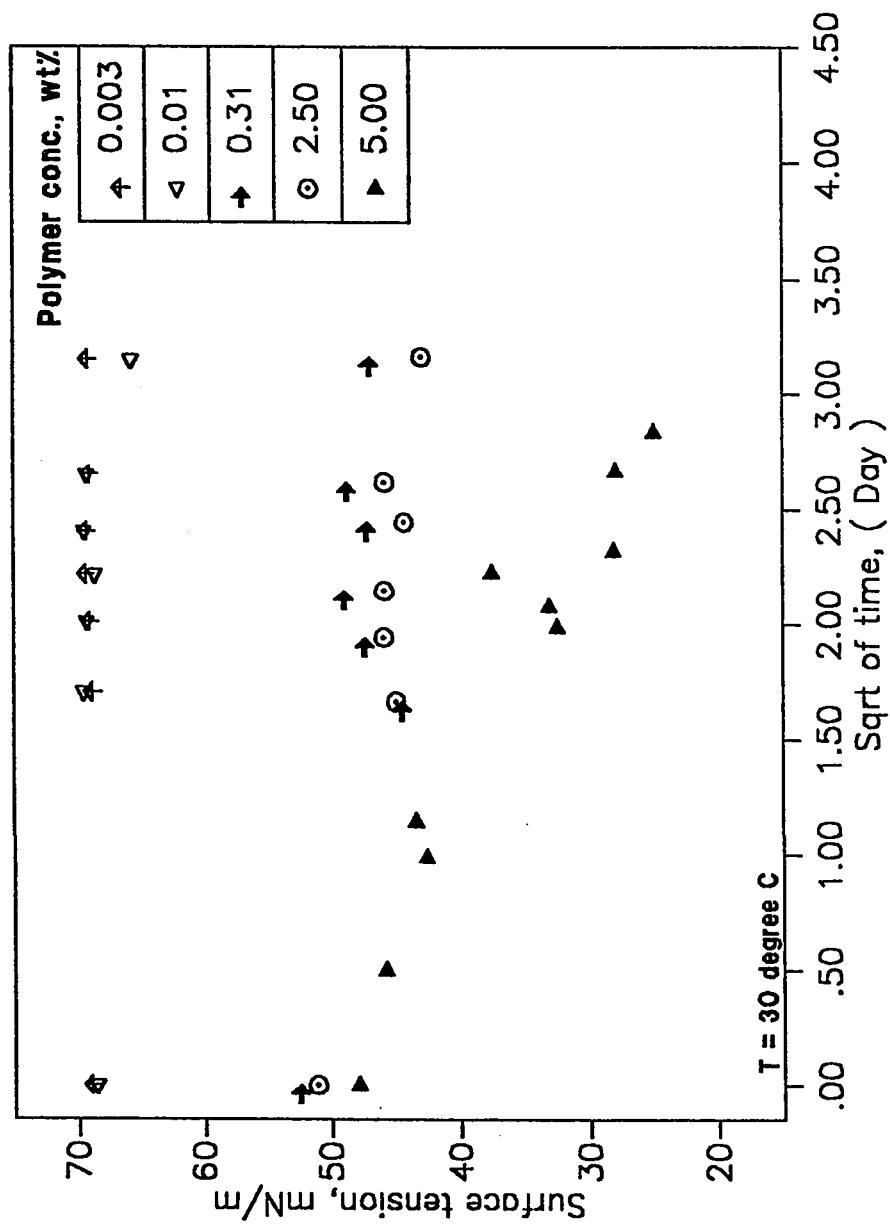


Figure 5.15: Variation of surface tension—sqrt of time relationship with polymer conc. for copolymer of maleic anhydride/1—hexadecene

### 5.4.3 Interfacial tension Behaviour of the Copolymers.

The oil-water interfacial tensions of the copolymers were determined using a Ring method. The detailed description of the procedure is given in chapter 3. N-decane was used in this study as the oil phase. The interfacial tensions (IFT) of the aqueous solution/decane were measured for two polymer concentrations, i.e 2.5 wt% and 5.0 wt% and for both polymers at different NaCl concentration ranging from 0 - 1.0wt% and all the measurements were performed at 40° C. The mixtures were left to equilibrate for a period of 2 1/2 months and maintained at 40° C, before the measurements of the IFT were taken .

The results of the measurements and interfacial tension behaviour with polymer concentration and NaCl salt concentration are depicted in tables 5.19 and 5.20 and figures 5.16 and 5.17. As expected, the IFT decreases as the polymer concentration increases from 2.5 to 5.0 wt%. Another very interesting feature observed for the two polymers is the decrease in IFT with increasing NaCl salt concentration.

The same explanation for the decrease in surface tension with increasing polymer concentration observed in the previous section also holds here for the decrease in IFT as the polymer concentration increases from 2.5 to 5.0 wt% . The decrease in IFT is due to the adsorption of the polymer molecules at the aqueous solution/decane interface. The increase in concentration of the polymer molecules at the aqueous solution-oil interface as the polymer concentration increases could be attributed to the amphiphilic structure of the copolymers. This consequently causes the reduction in IFT between the polymer aqueous



solution and oil (N-decane) [45]. This trend is observed for the two polymers under investigation and for all different polymer/NaCl salt solutions combinations considered. Similar observations were made by a number of workers in this area, such as Chou [5], Huang [46], and Sharma [3].

Furthermore, it is found that adding NaCl salt to the polymer solutions decreases interfacial tension of the polymer solutions. The IFT decreases with increasing NaCl concentration up to 1.0wt%. Beyond this the polymer precipitates. This behaviour could be attributed to the decrease in repulsion among the ionic (hydrophilic) groups such as  $O^- Na^+$ , present in the polymer structure, which allows a closer packing in the interfacial layer as the ionic strength is increased. The reduction in repulsive forces enhances the aggregation of micelles as the attractive forces between the micelles become predominant. In other words, this is consistent with the idea of intramolecular aggregation, and rationalizes as well the observed effects of added salts. Depressing the dissociation of the charged head groups and hence reducing their hydrophilicity, added salt enhances the interfacial activity of polyelectrolyte polymers, like the ones under investigation. However, this trend is usually not observed for nonionic polymer [100].

All these observations therefore explain why a sharp decrease in IFT is observed for the copolymers under investigation with increasing NaCl concentration. This behaviour is depicted for the two polymers in figures 5.16 and 5.17.

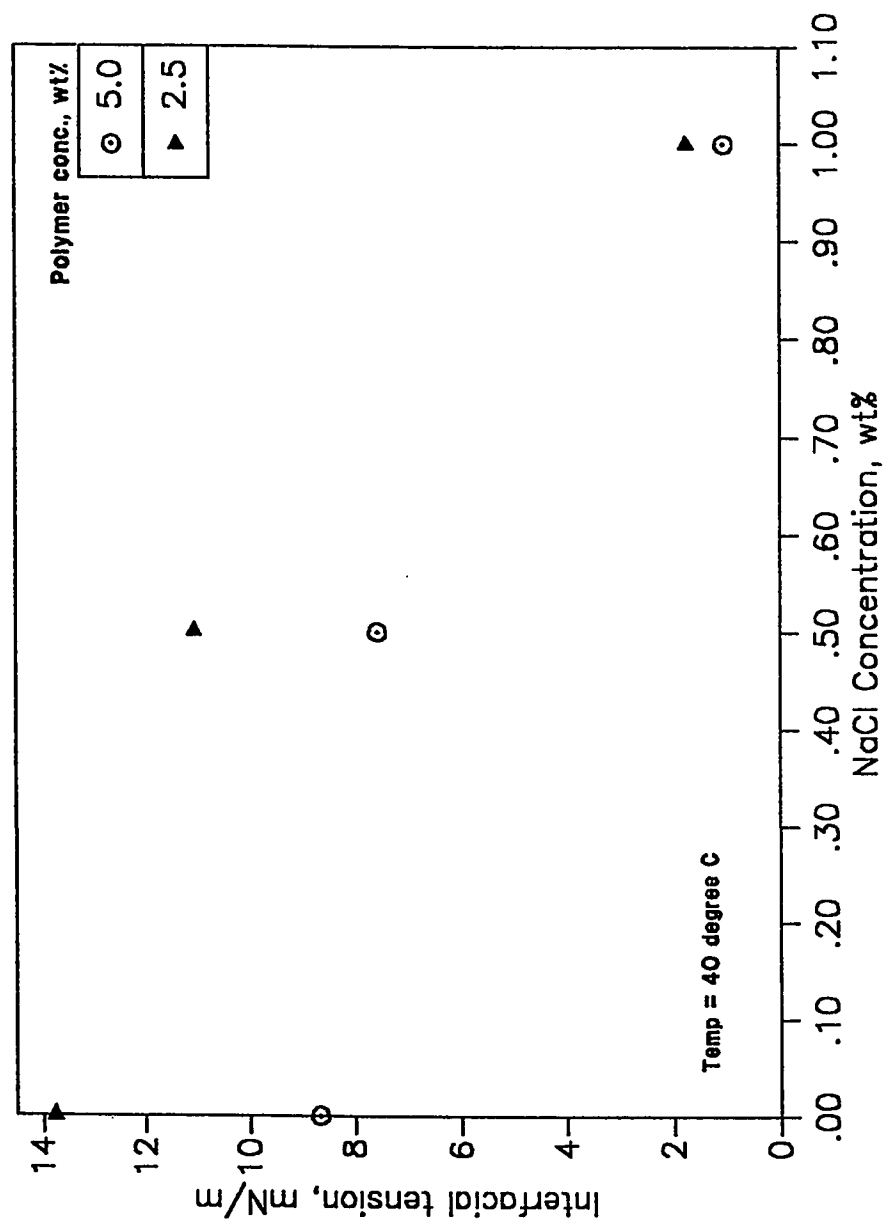


Figure 5.16 : Effect of NaCl salt on the Interfacial tension (polymer solution/decane) of copolymer of maleic anhydride/1-dodecene.

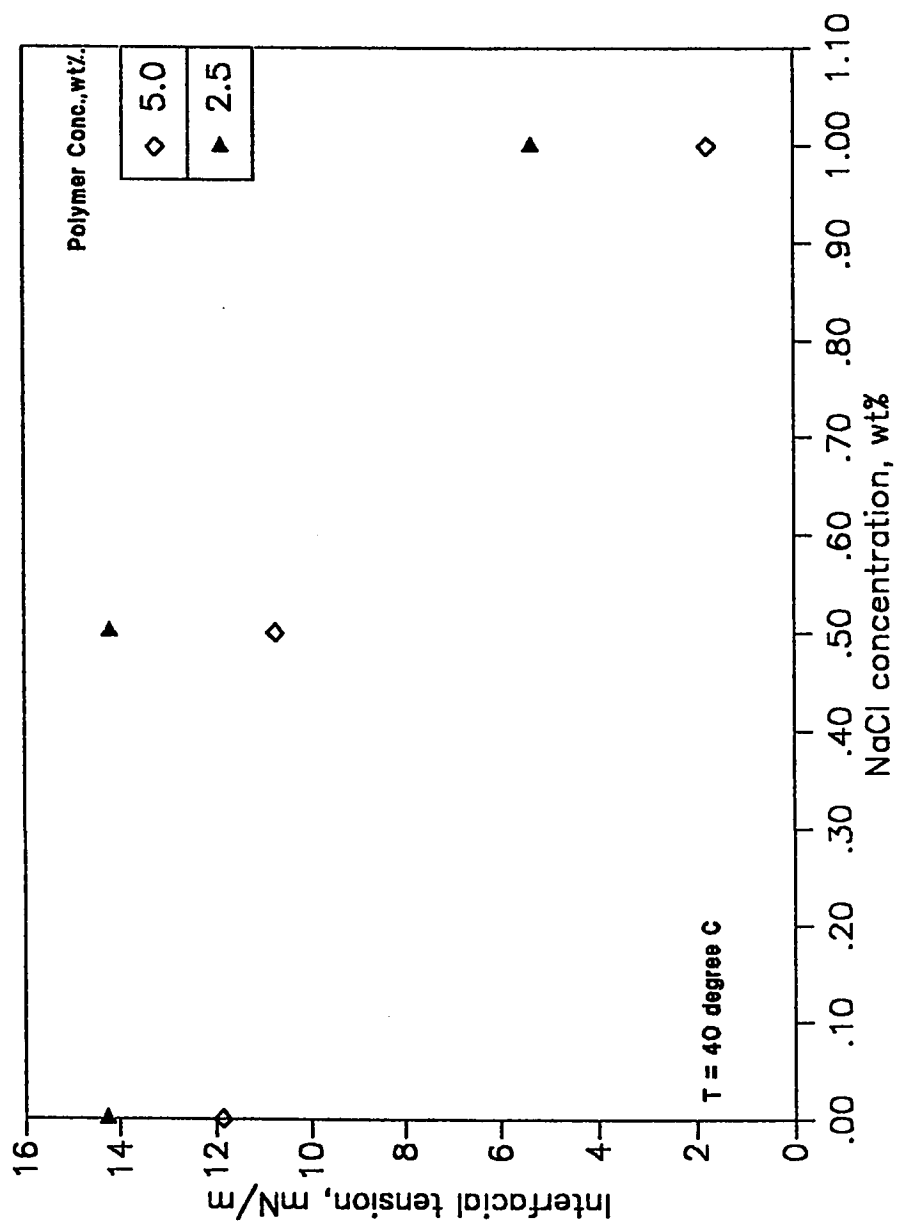


Figure 5.17 : Effect of NaCl salt on the Interfacial tension (polymer solution/decane) of copolymer of maleic anhydride/1-hexadecene

## 5.5 DISCUSSION AND CONCLUSIONS.

In general, the viscosity of the two copolymers is low, even at high polymer concentrations. For these polymers, the hydrophobic interactions are predominately intramolecular in nature, since intermolecular interactions would have resulted in a high rather than a low solution viscosity. In addition the two copolymers are of low molecular weight.

Furthermore, the copolymers exhibit relatively low salt tolerance in the range of 0 - 1.0 wt% NaCl salt concentration. In as much as the petroleum reservoir salinity can be very high, the copolymers should be designed for high salt tolerance.

The two copolymers also exhibit good surface and interfacial activities, including low surface and interfacial tensions (IFT). Although the surface tension and IFT of the copolymers are only moderate compared to conventional surfactants which exhibit ultimate surface tension and IFT values in the range of 20-40 mN/m and  $10^{-3}$  mN/m respectively. From these copolymers, surface tensions of 45 mN/m at CMC of 0.29 wt% is obtained for the copolymer of maleic anhydride/1-dodecene and 42.7 mN/m at CMC of 0.419 wt% is obtained for the copolymer of maleic anhydride/1-hexadecene. The ultimate IFT value obtained is in the range of 1mN/m.

Generally, the viscosity-shear rate relationship for the two copolymers exhibits a nearly constant viscosity at high shear rate. No shear thinning behaviour is exhibited.

Increasing the polymer concentration causes enhancement in the polymer solution viscosity. More of intrachain association of hydrophobic groups in the polymer structure is enhanced with increasing polymer concentration. The two copolymers also exhibit a reduction in viscosity with increasing temperature.

The relative invariance or a slight increase in viscosity with NaCl salt concentration is one of the attractive feature of these associative polymers. It also shows that the classical viscosity reduction of polyelectrolyte solutions in the presence of salts can be successfully prevented if the polyelectrolyte chain is grafted by a hydrophobic groups. In this case, hydrophobic groups aggregate all the more as ionic strength increases, leading to polymer chain association and consequently causes viscosity enhancement.

The copolymers also exhibit a decrease in surface tension with time at high polymer concentration, but invariant with time at low polymer concentration. Moreover, the copolymers exhibit a reduction in surface tension and interfacial tension with increasing polymer concentration. Evidence of more adsorption of the polymer molecules at the interface of oil-water is indicated.

It is found that adding NaCl salt to the polymer solution increases its interfacial activity. This behaviour is actually expected, since the polymers under investigation are polyelectrolyte polymers. The behaviour is another attractive feature of these polymers.

## **CHAPTER 6**

### **SYNTHESIS AND SOLUTION PROPERTIES OF HYDROPHOBICALLY-MODIFIED POLYVINYL ALCOHOL ( PVA ).**

#### **6.1 INTRODUCTION.**

Hydrophobically associating polymers are water-soluble polymers containing a small number of hydrophobic groups that promotes association in aqueous solutions [17]. As a consequence, these polymers exhibit thickening properties equivalent to those observed for higher molecular weight polymers. Furthermore, because of the anti-polyelectrolyte nature of some of these polymers, aqueous solutions of these hydrophobically associating polymers reduce salt sensitivity and other undesirable rheological properties found useful in chemical enhanced oil recovery processes [16,99]. Under increasing shear, the physical links between chains are disrupted but reform with decreasing shear. This way, it is possible to avoid the irreversible mechanical degradation which occurs for very high molecular weight polymers when subjected to high shear stresses [101].

Furthermore, the reversible association/dissociation process gives rise to particular rheological behaviours as a function of shear rate or shearing time. Such shear thinning and thixotropic properties are of great technological importance especially in applications on water-based systems which involve a viscosity control [21].

For the past few years, there has been an increasing interest in the synthesis and properties of hydrophobically modified water-soluble polymers. The

preparation of such materials can be carried out either by chemical modification of a pre-formed polymer or by copolymerization of the appropriate monomers or by a combination of both methods. The former synthesis route has mainly been applied to cellulose derivatives, poly(oxyethylene), which leads to the so called HEUR thickeners [98], i.e., hydrophobically modified ethoxylated urethane polymers, and more recently to poly(acrylic acid) [17]. The latter synthesis route has also been applied to copolymerize maleic anhydride with 1-alkene [61].

Based on the above synthesis route, i.e. chemical modification of a pre-formed polymer, polyvinylalcohol (PVA), can also be modified. Hydrophobically modified PVA can be obtained by reacting acid chlorides of long-chain fatty acids (hydrophobic groups) with PVA to form ester linkage. Some reactions of acid chlorides of long-chain acids and of other derivatives, with PVA have actually been investigated [65,66]. But mainly with the objective of producing materials of potential utility in surface coatings and in some cases for substrate materials for photographic systems.

This hydrophobically modified PVA can exhibit enhanced viscosification as a result of intermolecular hydrophobic interaction that occurs in the polymer aqueous solution, thus leading to the formation of polymolecular associations and hence increases hydrodynamic volume. Furthermore, as a result of the polymer amphiphilic structure, i.e. consisting of hydrophilic groups (hydroxyl and urethane groups) and hydrophobic moieties (long-chain fatty acid groups), the polymer is expected to exhibit high surface and interfacial activities. Amphiphilic molecules may form monomolecular or polymeric micelles in aqueous solution [17–19]. This formation of micelles enhances the polymer

ability to adsorb more at the interface. Thus this could lead to a very sharp reduction in surface and interfacial tensions of the polymer solution.

Detailed solution behaviours such as viscosity behaviour and surface and interfacial activities of the modified polymer for enhanced oil recovery applications have not been investigated at least to our knowledge. Although viscosity and surface tension behaviours of aqueous solution of unmodified PVA have been reported [67].

In the present study, chemical modification of PVA by esterification reaction of different combinations of long-chain fatty acid chlorides, such as decanoic acid chloride, docosanoic acid chloride and stearic acid chloride with PVA was carried out with the objective of investigating the modified polymer's viscosity and interfacial tension behaviours. The modification reaction was actually carried out on the urethanized PVA. This is because, it has been established that partly urethanized PVA is more stable and more soluble in solvents, such as water, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), [63]. The long-chain fatty acid chlorides were obtained from the reaction of fatty acid and thionyl chloride. The acid chlorides react readily with alcohols to form esters.

The hydrophobically modified PVA obtained in this work exhibits enhanced viscosification at moderate polymer concentration and also good surface and interfacial activities are exhibited by the polymer. Moreover the polymer displays high salt tolerance.



## 6.2 PREPARATION OF HYDROPHOBICALLY MODIFIED POLYVINYL ALCOHOL ( PVA ).

### 6.2.1 Preparation of Partly-Urethanized Polyvinyl alcohol ( PVA ).

Polyvinyl alcohol (PVA) with its free hydroxyl groups offers considerable latitude for chemical transformations such as esterification, etherification and acetalization. Partly urethanized PVA can be obtained by treatment of PVA with urea, in dimethylformamide (DMF) at 150° C, [63].

Partly urethanized PVA was prepared by treating PVA with urea having a degree of polymerization of 1600, and molecular weight of 72,000 and with degree of hydrolyzation of 97.5-99.5 mol% in distilled DMF at about 150° C. In a three-necked, 100 ml flask, equipped with a stirrer, a condenser, a thermometer and a magnetic stirrer were placed 10 g of the PVA, 50 g of distilled DMF and 13.65 g (1 mole urea to 1 base mole PVA monomer) of urea. The flask was maintained at a temperature of 148–152° C, under N<sub>2</sub> gas to stop O<sub>2</sub> free radicals degradation in the reaction mixture. The reaction mixture became homogeneous within a few minutes and proceeded, accompanied by evolution of gas. The reaction was left for 2 1/2 hours. After which, the resulting polymer was precipitated into methanol, purified twice in excess methanol, then dried in vacuo at 70° C until a constant weight is obtained.

The same procedure was similarly applied to urethanize the PVA with degree of polymerization of 2000, molecular weight of 100,000 and degree of

hydrolyzation of 86-89 mol%. Before the urethanization was carried out for this polymer, it was further hydrolyzed. The method of Bravar [68], was applied to hydrolyze the polymer. As an example: 10 g of the PVA was mixed with 200 ml of distilled water and then stirred with magnetic stirrer at room temperature. Then, 2 ml of 40% NaOH was added dropwise with continuous stirring. The reaction mixture was left in this condition for 24 hours. After which, the resulting polymer was precipitated in 500 ml methanol, purified twice in excess methanol, then dried in vacuo at 70° C until a constant weight of about 7.55 g is obtained.

### 6.2.2 Preparation of Fatty-acid Chlorides.

Three fatty-acid chlorides which include, Docosanoic acid chloride,  $(\text{CH}_3(\text{CH}_2)_{20}\text{COCl})$ , Stearic acid chloride,  $(\text{CH}_3(\text{CH}_2)_{16}\text{COCl})$ , and Decanoic acid chloride,  $(\text{CH}_3(\text{CH}_2)_8\text{COCl})$ , were prepared. The acid chlorides were obtained from the reaction of the fatty acid with thionyl chloride,  $(\text{SOCl}_2)$ .

As an example: 14 g of stearic acid,  $(\text{CH}_3(\text{CH}_2)_{16}\text{COOH})$ , was mixed with 12 ml of thionyl chloride and stirred with magnetic stirrer in a 100 ml, flask equipped with a condenser at 60° C. The reaction was accompanied with evolution of gas. The reaction was continued until the gas evolution ceased.  $\text{N}_2$  gas was blown into the reaction mixture to stop  $\text{O}_2$  free radicals degradation. This was continued until a constant weight is obtained. The same procedure was similarly applied to decanoic acid,  $(\text{CH}_3(\text{CH}_2)_8\text{COOH})$ , and obtained decanoic acid chloride and also applied to docosanoic acid,

$(\text{CH}_3(\text{CH}_2)_{20}\text{COOH})$ , to obtain the chloride of the acid.

### 6.2.3 Preparation of Modified Polyvinyl alcohol (PVA).

Different combinations and ratios of the three acid chlorides were reacted with the urethanized PVA, for both PVA of degree of polymerization of 1600 and 2000. Some of the modified polymers obtained were found insoluble in water even after heating to an elevated temperature for several hours. However, most of the modified polymers were soluble in water at ambient temperature. The different combinations of the hydrophobic side-chains of the urethanized polymers obtained and the results obtained from the polymers solution properties, such as solubility in water, viscosity and surface tension are given in table 6.1.

Example of one of the modification reactions is as follows: 4 g of the urethanized PVA having degree of polymerization of 1600 and molecular weight of 72,000 was mixed with 40 ml distilled DMF and heated to 140° C. It was maintained at this temperature until a clear homogeneous solution is obtained. After which, the three combination of the acid chlorides i.e 0.148g (0.5 mol% docosanoic acid chloride substitution), 0.125g (0.5 mol% stearic acid chloride substitution) and 0.157g (1.0 mol% decanoic acid chloride substitution) already mixed in a small test tube was introduced dropwise into the reaction mixture maintained at 140° C, and stirred vigorously. The reaction was carried out under  $\text{N}_2$  gas to stop  $\text{O}_2$  free radicals degradation. After 2 minutes of the reaction time, the resulting polymer was precipitated into methanol, purified twice in excess methanol, and then dried in vacuo at 70° C.

The same procedure was similarly applied with the same combination of the three acid chlorides to the urethanized PVA having degree of polymerization of 2000 and molecular weight of 100,000. Hydrophobically modified PVA were then obtained for this combination and other different combinations using the same procedure. The detailed reaction scheme and structure of the hydrophobically modified PVA are given in figure 6.1

**a, b, c, m, and n are repeats units**

Figure 6.1 : Reaction schemes and molecular structures of modified Polyvinyl alcohol (PVA).

**Table 6.1: The Viscosity(at shear rate of 0.8(1/sec)), Surface tension and Solubility Data of Modified PVA with Different Combinations of Hydrophobic Groups measured at 30 degrees C.**

C22 mol%	C18 mol%	C10 mol%	CONC wt%	VISCOSITY (cps)	S.T mN/m	SOLUBILITY in water
0.5	0.5	1.0	0.5	30.1	48.85	soluble
0.5	1.5	1.0	0.5	25.0	52.61	soluble
1.5	0.5	1.0	0.5	20.0	49.63	soluble
1.5	1.5	1.0	0.5	15.0	50.13	soluble
1.0	1.0	2.0	0.5	25.0	57.65	soluble
0.5	0.5	3.0	0.5	30.1	55.88	soluble
1.5	1.5	3.0	0.5	30.1	54.28	cloudy
1.5	0.5	3.0	0.5	35.1	52.08	cloudy
0.5	1.5	3.0	0.5	40.1	53.46	cloudy
2.0	0.5	0.5	0.5	50.1	52.51	cloudy
2.0	0.0	0.5	0.5	20.1	54.44	soluble

**Table 6.1: Continues.**

0.5	0.5	0.5	0.5	****	*****	insoluble
0.5	1.5	0.5	0.5	****	*****	insoluble
0	2.0	1.0	5.0	2740	28.05	soluble
0	2.0	2.0	5.0	1085	24.15	cloudy
0	0.5	1.0	5.0	34.1	38.43	soluble
0	2.0	0	5.0	165.1	52.00	cloudy
0	1.0	0	3.8	149	53.74	cloudy
0	0	0	5.0	120	43.89	soluble
0	0	5.0	5.0	16.0	31.90	cloudy

where

C22 = Docosanoic acid hydrophobic group

C18 = Stearic acid hydrophobic group

C22 = Decanoic acid hydrophobic group

ST = Surface tension

### 6.3 POLYMER CHARACTERIZATION.

#### 6.3.1 Elemental Analysis.

Elemental analysis to determine carbon, hydrogen and nitrogen content of the urethanized and hydrophobically modified polyvinyl alcohol ( PVA ) was conducted at the central analytical laboratory of K.F.U.P.M, research institute. The analytical data obtained are given in table 6.2.

From the result of the elemental analysis, the degree of urethanization, DU, in mol% was calculated based on N% obtained and obtained 15.4 mol% and 33.3 mol% for urethanized PVA with molecular weight of 72,000 and 100,000 respectively. The degree of urethanizations obtained for the two polymers are unusually high atleast when compared to what has been reported [63], for these kinds of polymers. The high degree of urethanization could be attributed to the different reaction conditions followed in this work. Essentially, the procedure of Sakurada [63], was applied, with the introduction of  $N_2$  gas to stop  $O_2$  radicals degradation.



**Table 6.2: Elemental Analysis of the Urethanized, Hydrolyzed and Some of the Hydrophobically Modified Polyvinylalcohol (PVA)**

Polymer	%C	%H	%N
I	49.6	8.70	4.2
II	46.5	8.60	ND*
III	43.9	8.00	8.0
IV	49.9	8.50	1.4
V	48.5	8.70	3.3
VI	47.9	8.30	3.6
VII	49.0	8.90	3.0
VIII	47.2	8.70	2.9

where

I = Urethanized PVA of molecular weight of 72,000.

II = Hydrolyzed PVA of molecular weight of 100,000

III = Urethanized PVA of molecular weight of 100,000.

IV = Modified PVA (0.5mol%C22,0.5mol%C18&1.0mol%C10) with MW of 72,000.

V = Modified PVA (0.5mol%C22,0.5mol%C18&1.0mol%C10) with MW of 100,000.

VI = Modified PVA (2.0mol%C22,0.5mol%C18&0.5mol%C10) with MW of 100,000.

VII = Modified PVA (2.0mol%C18 & 1.0mol%C10) with MW of 72,000.

VIII = Modified PVA (2.0mol%C18 & 2.0mol%C10) with MW of 72,000.

and

ND\* = Not present

#### 6.4 POLYMER PROPERTIES.

The solution properties, such as viscosity behaviour, surface and interfacial activities of the hydrophobically modified polyvinyl alcohol (PVA) were investigated with respect to polymer concentration, polymer molecular weight, temperature, salinity, ageing and effect of the modification for a wide range of shear rates.

In this study, concentrated stock solutions were prepared at least 24 hours before use. Final solutions of the desired composition were obtained by dilution of the appropriate stock solution with water and, if necessary, addition of appropriate amount of solid NaCl. Most of the dissolution processes took 2-3 days. The viscosity and surface tensions of all the modified polymers obtained in this work are displayed in table 6.1. As an example of dissolution: 5 g (5 wt%) of the modified PVA with the three hydrophobic substitutions of 0.5 mol%C22, 0.5 mol%C18 and 1.0 mol%C10 was dissolved in 95 ml of distilled water by stirring for 2 days at ambient temperature. After which the polymer

dissolved completely. This was the stock solution. Subsequent compositions, such as 2 wt%, 0.5 wt% e.t.c were obtained from appropriate dilution of the stock solution. The same procedure was similarly applied for the other modified PVA obtained in this work.

From all the modified PVA obtained with different combinations of the hydrophobic groups i.e acid chlorides, as shown in figure 6.1, the one with 0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10 degree of substitutions was studied in detail. The solution properties of this polymer were studied in detail because it is the one that gives the lowest surface tension, high viscosity and completely soluble in water. The modified polymer with hydrophobic combination of 2.0 mol%C18 and 1.0 mol%C10 is also chosen for study in this work, because of its highest viscosity, low surface tension and completely soluble in water. Others were either found insoluble in water, or displaying undesirable solution properties. For example, as displayed in figure 6.1, the hydrophobically modified polymers with only C18 hydrophobic group were found cloudy in aqueous solution, while those with both C18 and C10 hydrophobic groups were found soluble in water. The cloudy formation or the insolubility exhibited in the former is probably due to the imbalance between hydrophobic and hydrophilic forces on the polymer main chain. The solubility exhibited in the latter could be attributed to the balance between hydrophobic and hydrophilic forces on the polymer backbone. The solution properties of the modified PVA chosen for study were investigated for both modified PVA with molecular weight of 72,000 and 100,000.

#### 6.4.1 Viscosity Behaviour of Hydrophobically

##### Modified Polyvinyl alcohol ( PVA ).

The solution viscosity of the hydrophobically modified polyvinyl alcohol (PVA) was determined using a digital Brookfield viscometer with UL adapter accessories or SC4-18 spindle accessory whichever is appropriate at shear rate ranging from  $0.4$  to  $79.4 \text{ s}^{-1}$ . All viscosities for the polymer concentration ranging from  $0.5 \text{ wt\%}$  to  $5.0 \text{ wt\%}$  were measured at temperature of  $30 - 70^\circ \text{ C}$ . The results of the measurement obtained are given in tables 6.2-6.12.

Tables 6.2-6.12 and figures 6.2-6.12 show the effects of polymer concentration, temperature, NaCl salt concentration, polymer modification, ageing, shear rate, and molecular weight on the Brookfield viscosity of the hydrophobically modified PVA with hydrophobic substitution of  $0.5 \text{ mol\%C22}$ ,  $0.5 \text{ mol\%C18}$  &  $1.0 \text{ mol\%C10}$ . As shown in figure 6.2, the hydrophobically modified PVA exhibits a greater viscosity than the unmodified PVA i.e original and urethanized PVA . The incorporation of the hydrophobic groups is the primary factor causing the enhancement of the viscosity by promoting intermolecular hydrophobic association. As a result of this interchain interactions, which leads to increase in hydrodynamic volume and consequently causes increase in the viscosity of the modified polymer. This then indicates that hydrophobic interactions occur between chains, which leads to polymolecular structures with large hydrodynamic radius. The enhanced viscosity obtained for the hydrophobically modified PVA is consistent with studies reported in the literature for hydrophobically associating polymers [4,12,17 – 20]. On the other hand, unmodified PVA is observed to decrease in viscosity after being

urethanized.

For the modified PVA under investigation, an almost shear rate independent viscosity is observed at high shear rate as shown in figures 6.2, 6.4 and 6.11 . However, at low shear rates, a typical shear thinning behaviour appears as depicted in figures 6.2, 6.4, 6.6, 6.8, 6.9 and 6.11 for both polymers of molecular weight of 72,000 and 100,000.

The characteristic almost constant viscosity and the shear-thinning behaviours exhibited by the polymer are probably due to the orientation and disentanglement of the macromolecular chains under shear. The decrease in viscosity with increasing shear rate, i.e shear thinning behaviour, corresponds to the progressive rupture of the intermolecular associations upon increasing the shear rate. Similar trend was observed by Kaczmariski et.al [98], and Hill et.al [99], in their studies.

The hydrophobically modified PVA also exhibits a sharp increase in viscosity with increasing polymer concentration for all the shear rates considered and for both polymers of molecular weight of 72,000 and 100,000 at 30° C. This behaviour is displayed in figures 6.3-6.6.

The behaviour is due to the formation of large aggregates, as the polymer concentration is increased. This behaviour is expected because at low polymer concentration, the hydrophobic chains have little chance of interacting with each other, thus leading to formation of small aggregates with a small hydrodynamic radius. However, as the polymer concentration is increased, more of hydrophobic intermolecular interactions are probably occurring, which leads to

the formation of large aggregates, i.e. polymolecular structures, with a high hydrodynamic volume and consequently high solution viscosity [17 – 19,98 – 99].

The development of viscosity behaviour for associative polymers like the one under investigation relies on an increase in the apparent macromolecular weight due to cooperative intermolecular aggregation among hydrophobic groups or moieties with increasing polymer concentration. Under high shear condition, the hydrophobic interactions can be disrupted resulting in a decrease in the apparent molecular weight hence a decrease in solution viscosity. However, under low shear conditions the hydrophobic interchain associations may again form, lending much higher viscosity fluids [25,26].

Figures 6.7-6.9 show the effect of temperature on the solution viscosity of the modified polymer. A sharp decrease in solution viscosity is observed with increasing temperature.

Figure 6.11 depicts the effect of polymer molecular weight on the viscosity of the modified polymer. The modified polymer with molecular weight of 100,000 is observed to substantially enhances viscosity. A sharp increase in solution viscosity is actually observed as the molecular weight of the polymer is increased from 72,000 to 100,000 for the same polymer concentration of 4.0 wt% and for all the shear rates considered . This behaviour is observed for the polymer at 30° C.

This behaviour is actually expected and could be attributed to the increase in size of the polymer molecules as the molecular weight is increased, which leads to a higher hydrodynamic volume and consequently to the enhancement in

the viscosity. Actually enhanced thickening ability for associative polymers like the one under investigation relies on an increase in the apparent macromolecular weight due to cooperative intermolecular aggregation among hydrophobic moieties. [25,26].

Figure 6.10 shows the effect of NaCl concentration on the solution viscosity of the modified polymer with molecular weight of 72,000. The polymer was found salt tolerant up to 7.0 wt% of NaCl concentration. Beyond this concentration, a precipitate was observed. Within this range, i.e 0-7 wt% NaCl concentration and for shear rate of 36.7 and 73.4 s<sup>-1</sup>, an insignificant changes in viscosity with increasing NaCl concentration is observed. A maximum is observed at about 1.0 wt% NaCl concentration, and a minimum at about 2.0 wt% NaCl concentration. Above 2 wt% NaCl concentration, an increase in viscosity is observed up to about 4.0 wt% NaCl concentration and then levels off as the NaCl concentration is increased further.

The relative invariance of viscosity to changes in salt concentration as depicted in figure 6.10 is one of the attractive feature of this hydrophobically modified polymer. Adding salt to the modified polymer is probably promoting intermolecular association among the hydrophobic groups in the polymer structure, thus enhancing viscosification ability of the polymer. The relative invariance of the viscosity to changes in salt concentration could not have been due to the charge shielding effect on the electrostatic repulsive forces among the ionic groups, since the polymer under consideration is a non polyelectrolyte polymer, as such there are no any charges on the polymer structure that could have probably causes the reduction in the electrostatic repulsive forces of the

polymer.

Figure 6.12 depicts the effect of ageing on the solution viscosity of the modified PVA with molecular weight of 72,000. This was performed by measuring viscosity of the polymer at a week interval for about 5 weeks. The polymer solution viscosity was measured at 30° C. The viscosity of the polymer was observed to decrease slightly with time. This could be attributed to the instability of the polymer , which is probably due to the weakness of the ester linkage in the polymer structure.



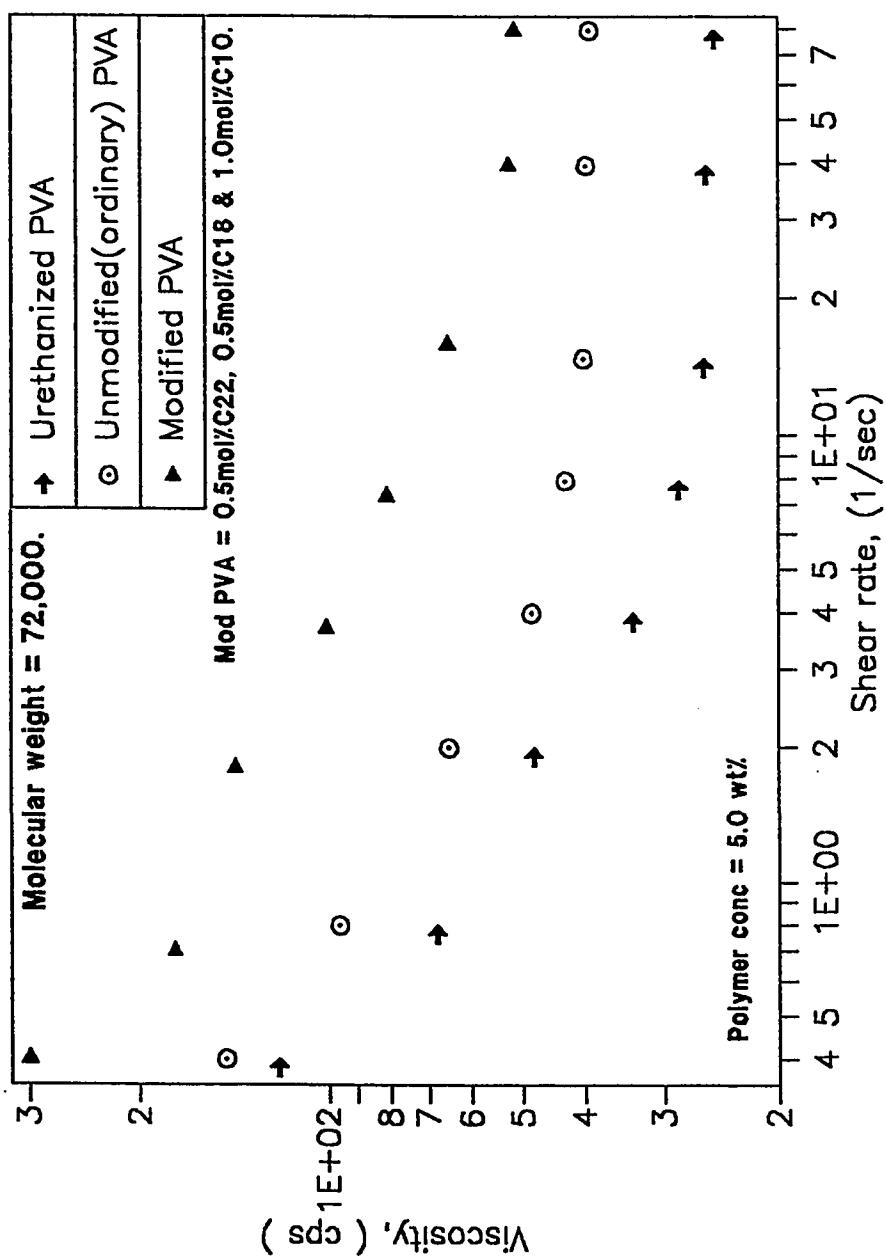


Figure 6.2: Variations of viscosity—shear rate relationship for modified, urethanized and ordinary PVA at 30 degree C.

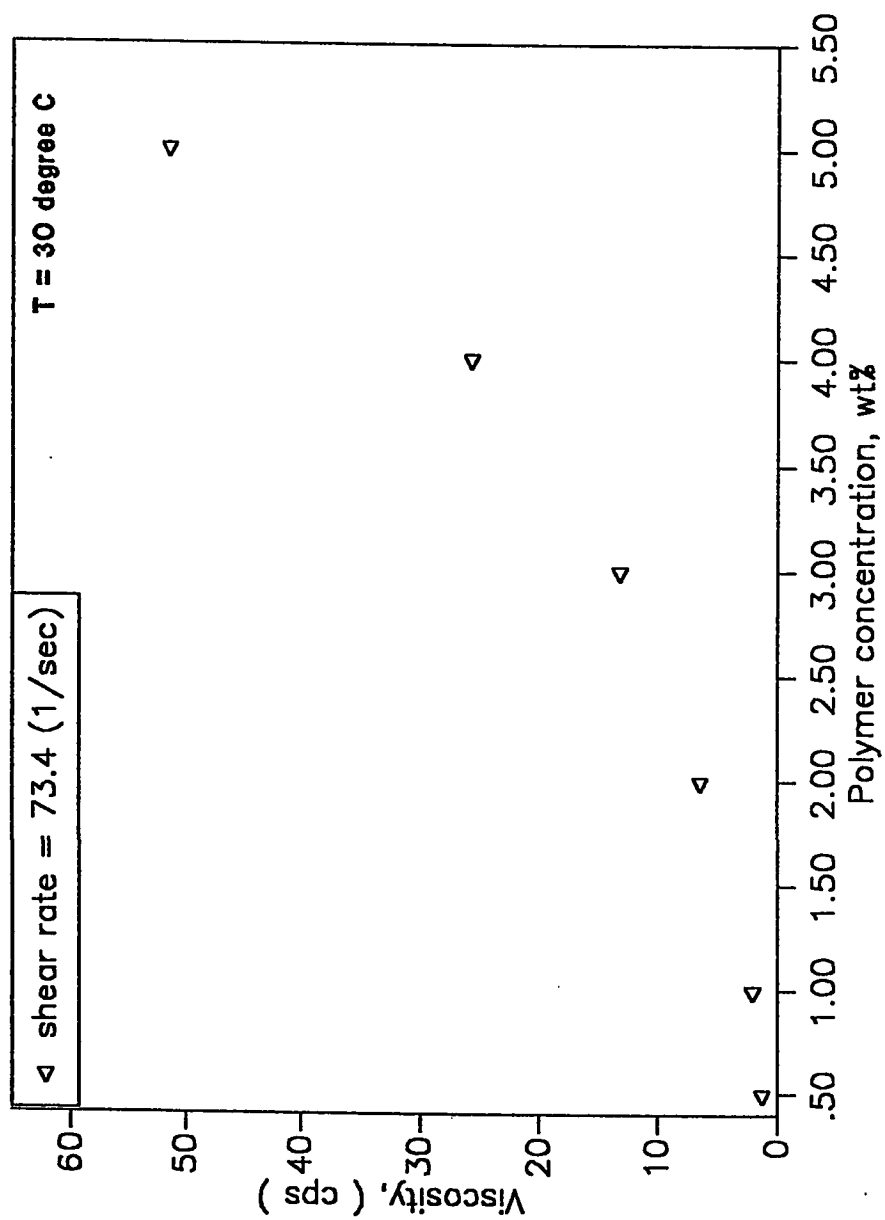
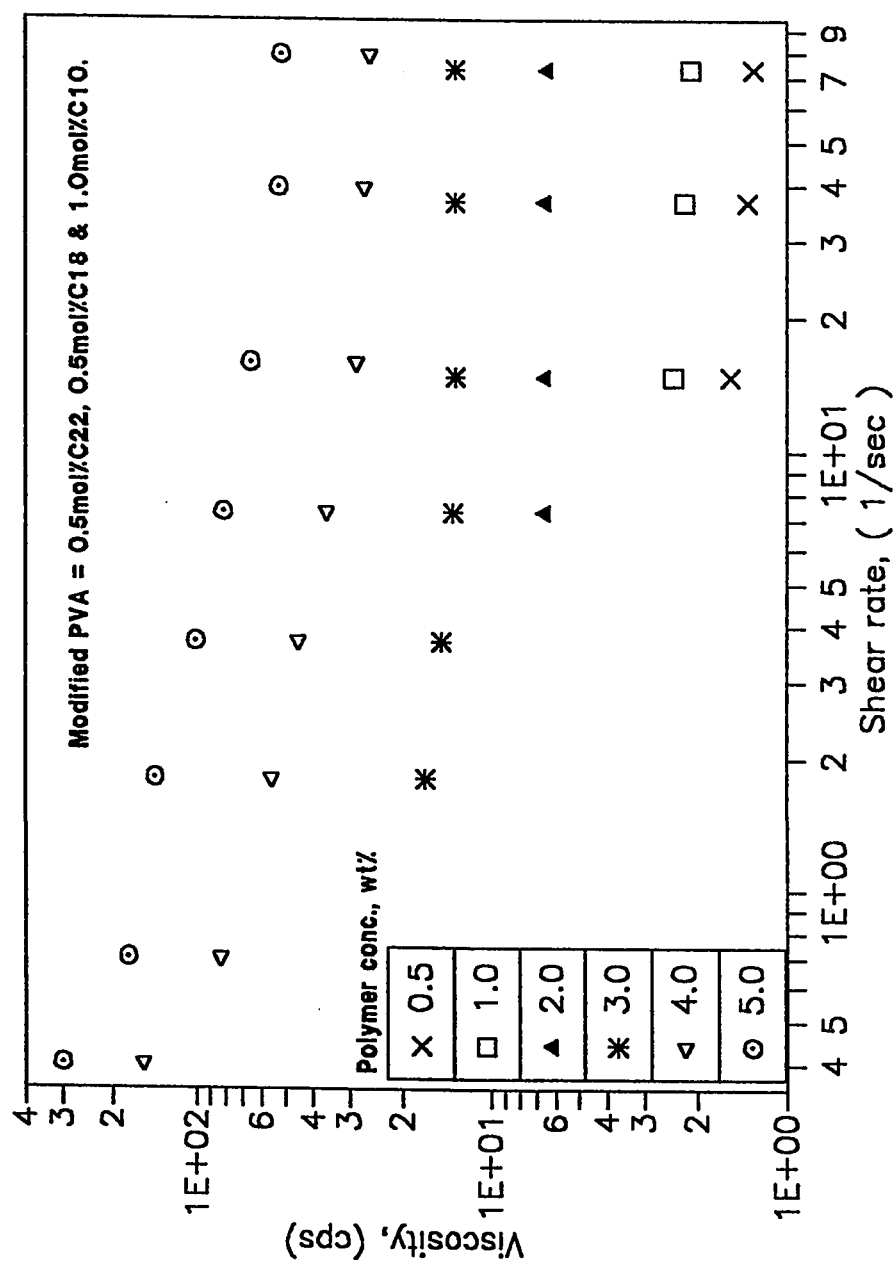


Figure 6.3 : Effect of Polymer conc. on the viscosity of modified PVA (0.5mol%C22, 0.5 mol%C18 & 1.0 mol%C10) with MW of 72,000.



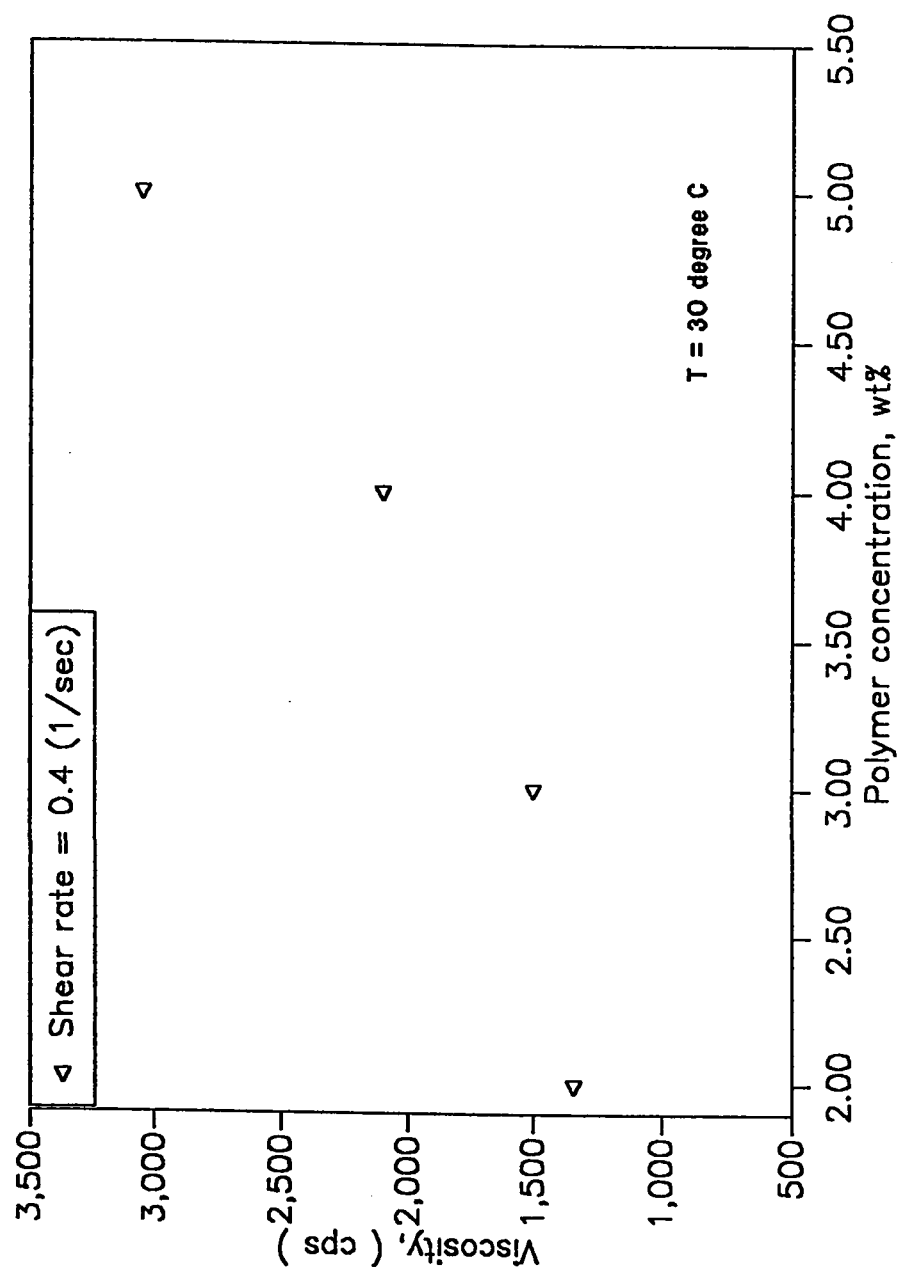


Figure 6.5 : Effect of Polymer conc. on the viscosity of modified PVA (0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10) with MW of 100,000.

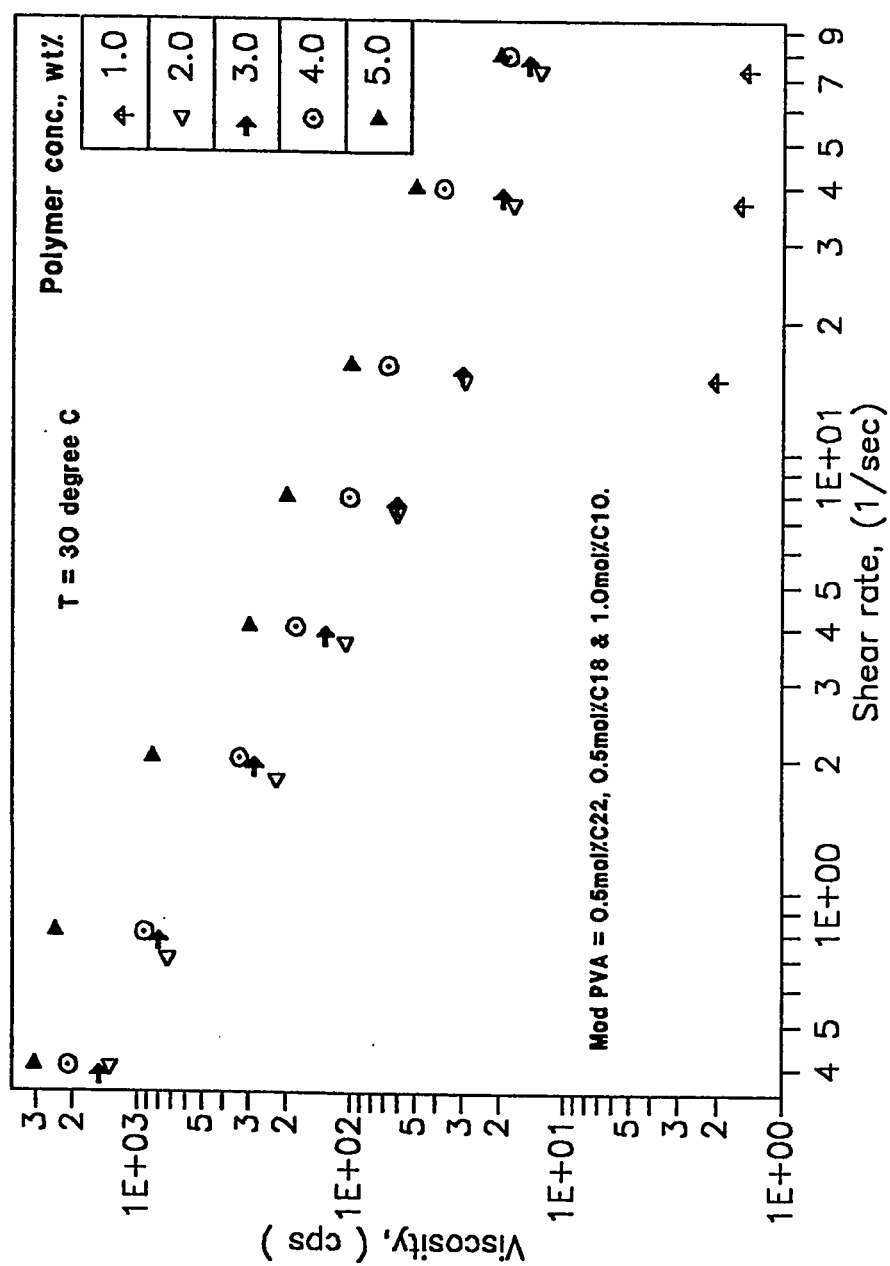


Figure 6.6 : Variations of viscosity-shear rate relationship with polymer concentration for modified PVA with MW of 100,000.

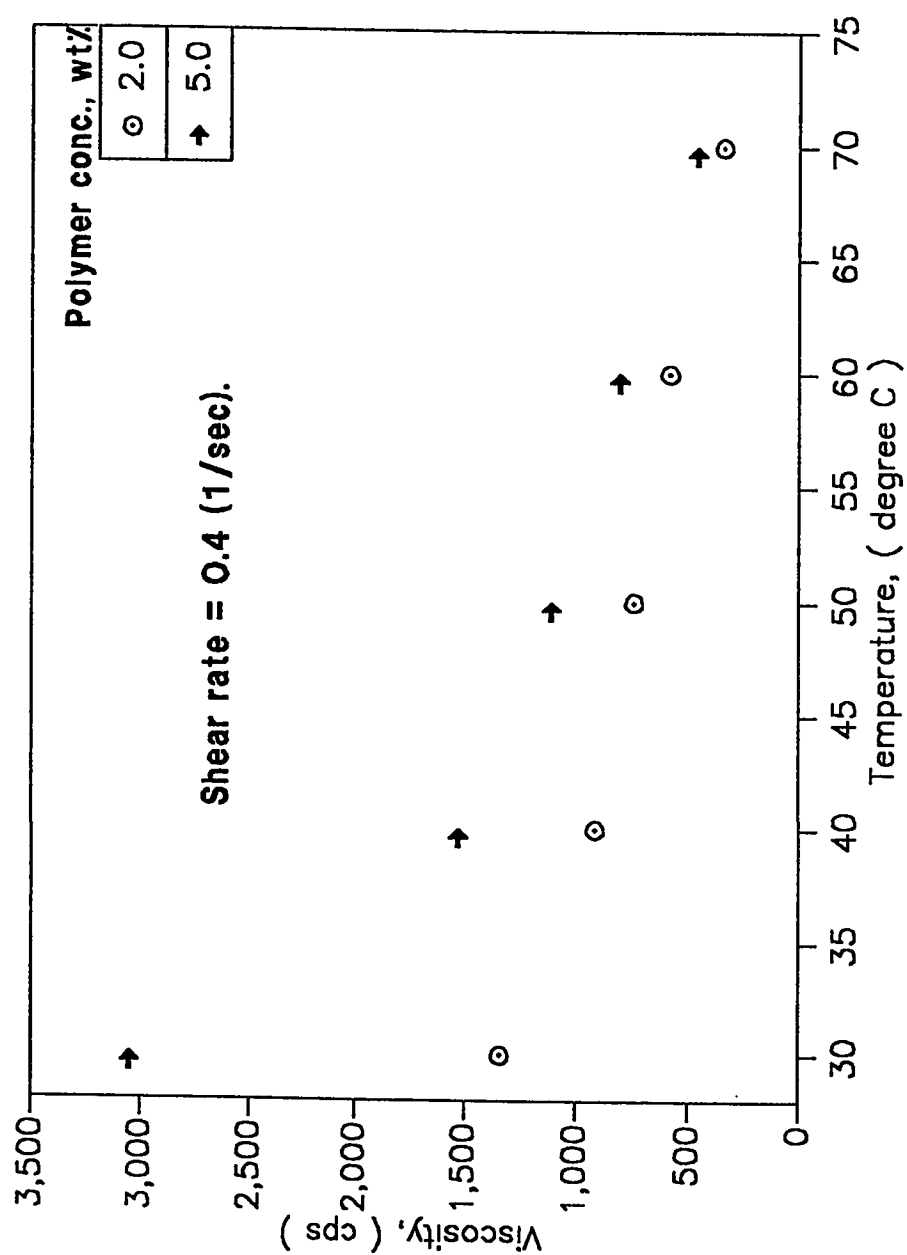


Figure 6.7 : Plots of viscosity versus temperature for modified PVA (0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10) with MW of 100,000.

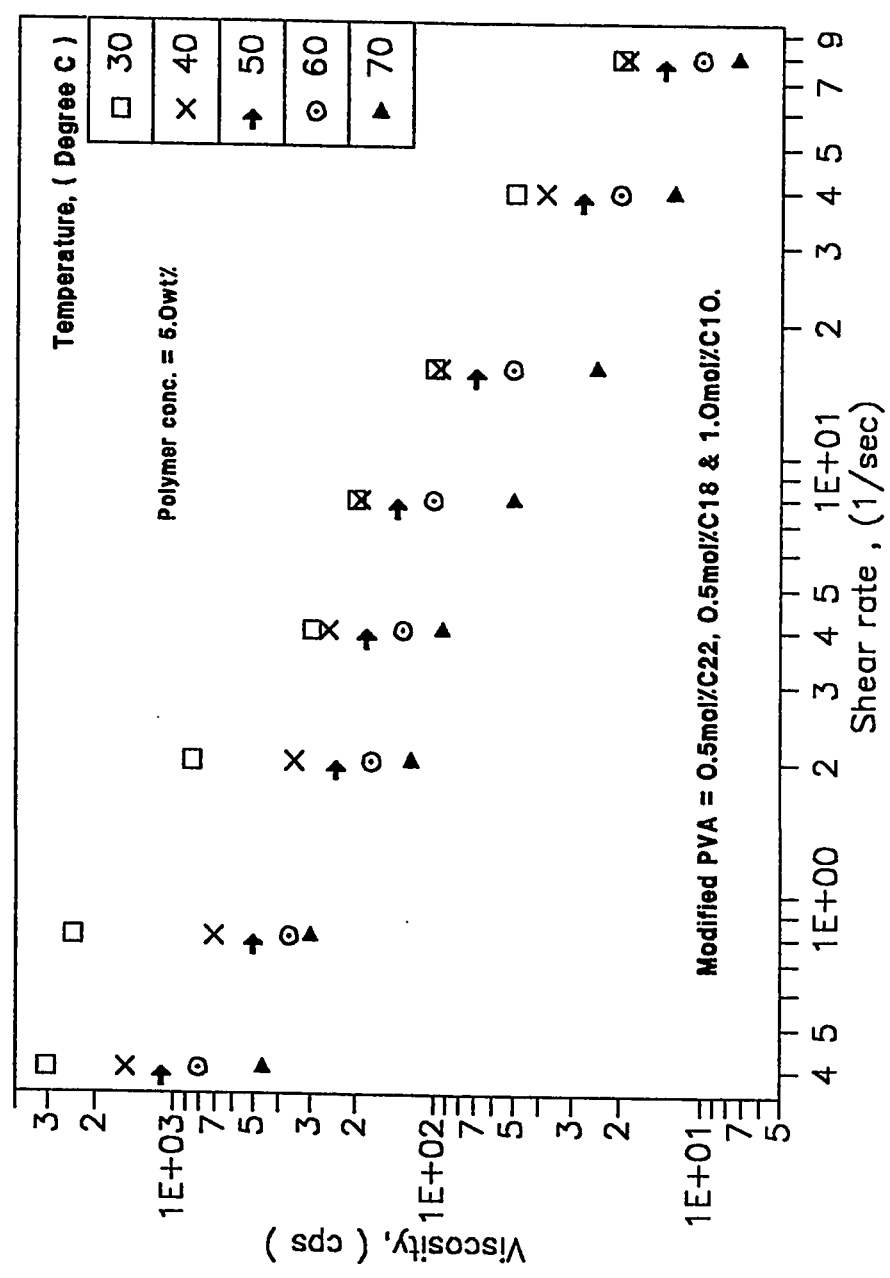


Figure 6.8 : Variations of viscosity—shear rate relationship with temperature for modified PVA of MW of 100,000 .

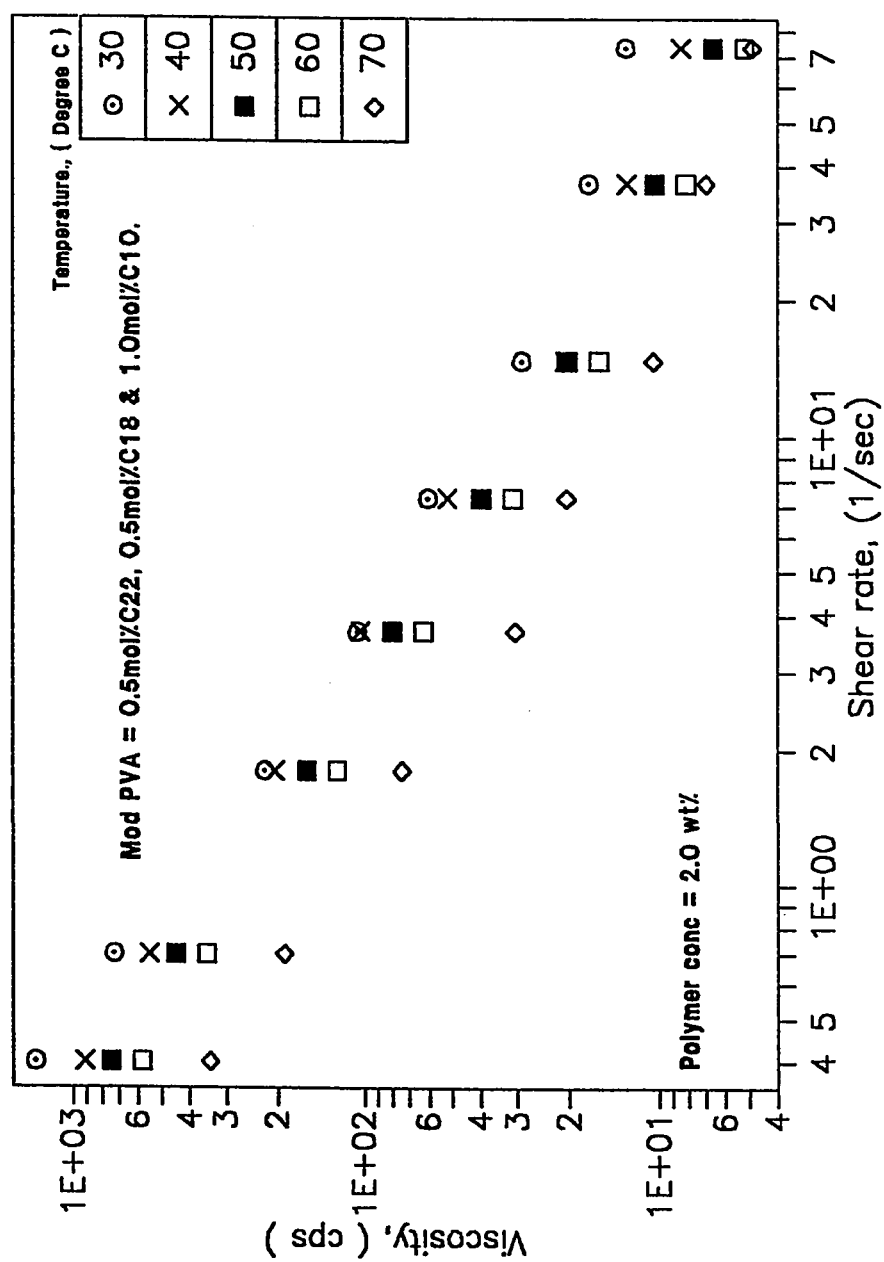


Figure 6.9 : Variations of viscosity-shear rate relationship with temperature for modified PVA with MW of 100,000 .



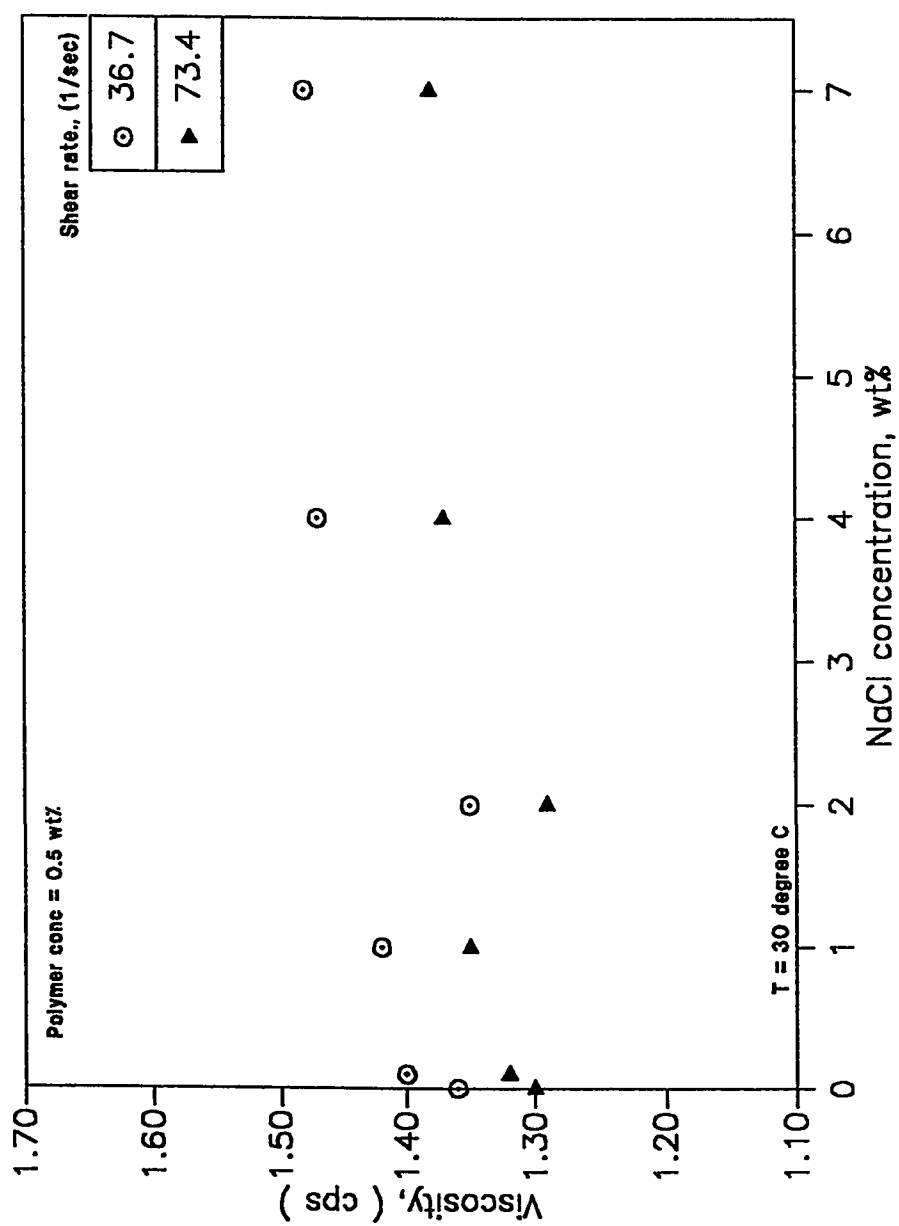


Figure 6.10 : Effect of NaCl on the viscosity of modified PVA (0.5 mol% C22, 0.5 mol% C18 & 1.0 mol% C10) with MW of 72,000.

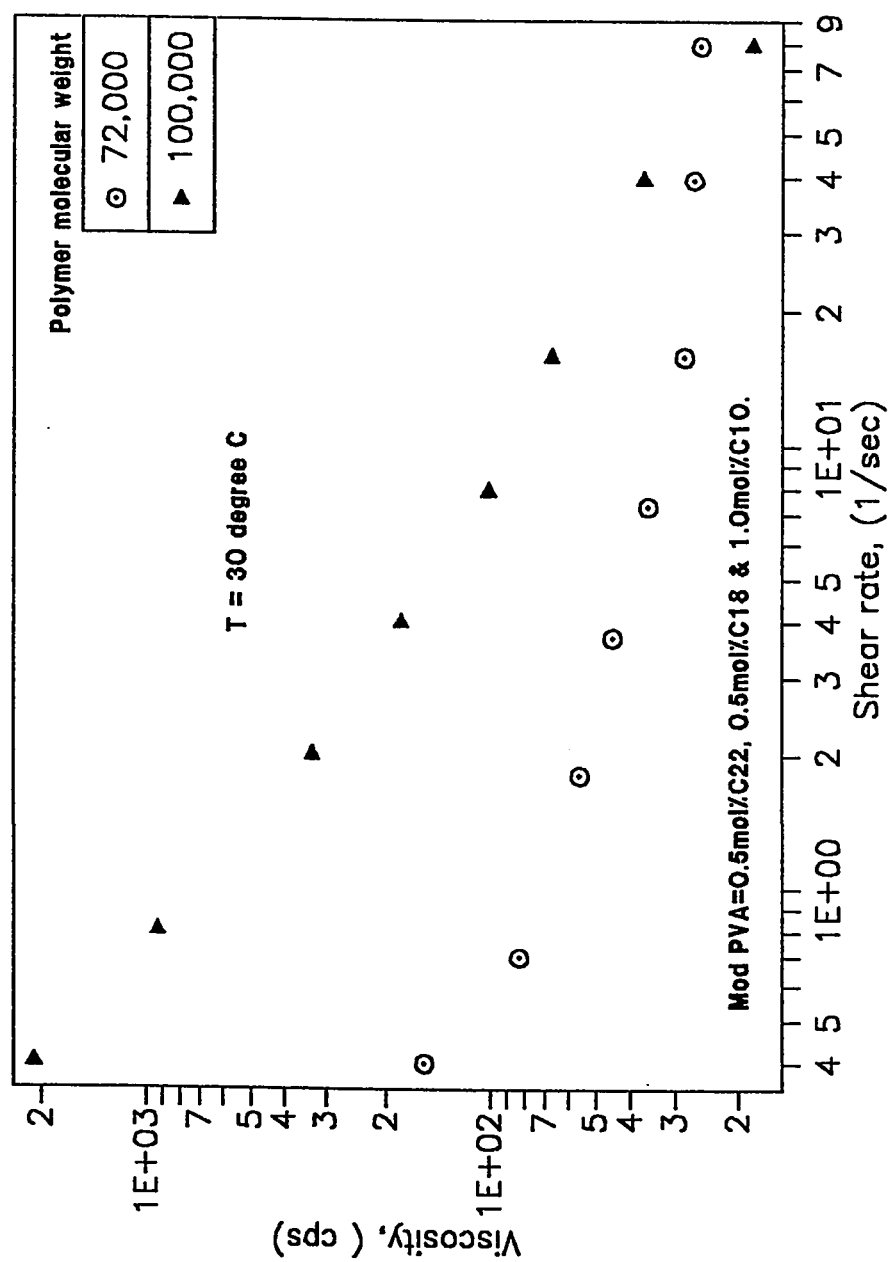


Figure 6.11 : Variations of Viscosity—shear rate relationship with molecular weight for modified PVA for polymer conc. of 4.0 wt%.

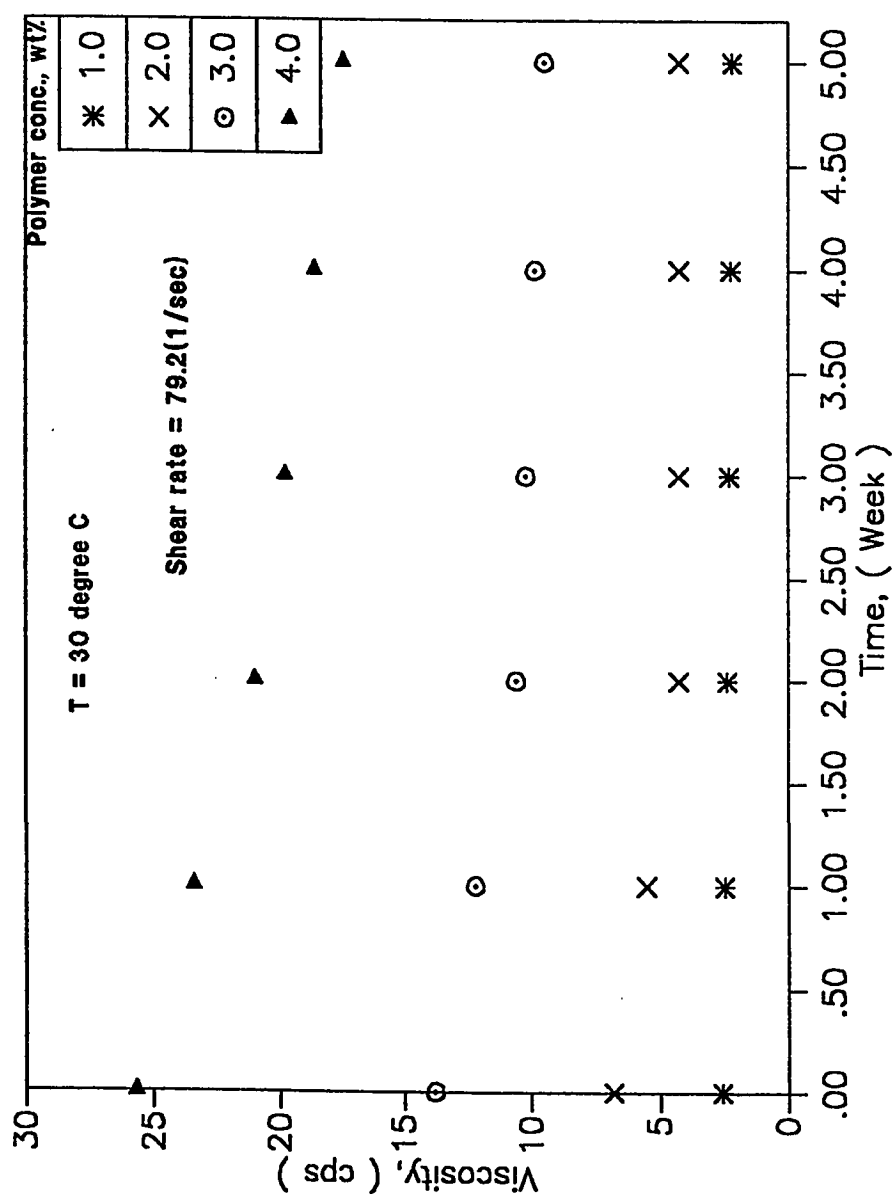


Figure 6.12 : Effect of Ageing on the viscosity of Modified PVA (0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10. ) with MW of 72,000.

#### 6.4.2 Surface tension Behaviour of Hydrophobically

##### Modified Polyvinyl alcohol ( PVA ).

The surface tension of the modified polymer was determined using the plate method. All measurements for different polymer concentrations were performed at 30° C. The surface tension was also measured for polymer concentration of 0.5 wt% with different NaCl concentrations ranging from 0.1 to 7.0 wt% . The detailed description of the surface tension measurement procedure is given in chapter 3.

Tables 6.13-6.17 and figures 6.13-6.20 depict the effects of the polymer modification, polymer concentration, NaCl concentration, time and molecular weight on the surface tension of the modified polymer. As shown in figure 6.13, the hydrophobically modified PVA exhibits a higher surface activity than the unmodified PVA, i.e original and urethanized PVA. The surface tension of the modified polymer is observed to be lower than the unmodified PVA and also observed to decrease with increasing polymer concentration. The incorporation of the hydrophobic groups is the primary factor causing this higher surface activity.

This phenomenon could be attributed to the amphiphilic structure of the modified PVA, i.e containing both hydrophobic groups, (long-alkyl chains) and hydrophilic groups (hydroxyl and urethane groups), which the unmodified PVA do not possess.

Furthermore, urethanized PVA is also observed to exhibit more surface activity than the original PVA. Due to this surface activity of the urethanized

PVA, the surface tension of the urethanized PVA is lower than that of original PVA. However, the surface tension of the modified PVA is much lower than those of urethanized and original PVA.

The high surface activity displayed by the urethanized PVA could be attributed to the urea groups attached, which probably enhances the polymer molecules tendency to adsorp more at the air-aqueous solution interface, thus causes reduction in surface tension.

As shown in figures 6.14-6.17, a sharp decrease in surface tension is observed with increasing polymer concentration for both polymers of molecular weight 72,000 and 100,000. As the polymer concentration increases, surface tension is lowered. For this polymer, no critical micelle concentration, (CMC) or break point resembling a CMC is observed in contrast to oligomeric polymer already investigated [48]. The surface tension decreases throughout the range of polymer concentrations considered.

As the polymer concentration increases, the surface tension decreases because of adsorption of the polymer molecules at the air-aqueous solution interface. Actually the higher the polymer concentration, the larger the adsorption (adsorbed molecules are in equilibrium with bulk dissolved ones) and the lower the surface tension [83]. This behaviour could be attributed to the amphiphilic structure of the polymer, which probably causes increase in concentration of the polymer molecules at the air-aqueous solution interface, thus causes the reduction in surface tension [45].

The surface tension of the hydrophobically modified polymer is also

observed to be time-dependent. The time-dependence of surface tension for the polymer of molecular weight of 72,000 is displayed in figure 6.18. A maximum in surface tension is observed at about 6th-8th days of measurement. After which, a decrease in surface tension is observed from 8th up to 15th days of the measurement. This behaviour is observed for all the polymer concentrations considered at 30° C.

The decrease in surface tension of the modified polymer with time could be attributed to the surface reorientation process of hydrophobic moieties from the bulk phase to the air-aqueous solution interface. Extensive equilibration times may also be required due to slow diffusion or perhaps due to conformational changes behaviour of the polymers [100]. Similar trends have also been observed by Okubo [37], and Ishimuro [52].

Furthermore, it is observed that adding NaCl to the polymer solution increases its surface activity. The surface tension is observed to decrease drastically with increasing NaCl concentration up to 7.0 wt%. Beyond which, a precipitate formation was observed. The behaviour is depicted in figure 6.19 for the modified polymer of molecular weight of 72,000 and polymer concentration of 0.5 wt%.

This behaviour of the polymer with NaCl is an interesting feature of the polymer, as the polymer can be suited for petroleum reservoir with high salinities. The behaviour could be attributed to the increase in adsorption of the polymer molecules at the air-aqueous solution interface as the NaCl is added. In essence NaCl is promoting increase adsorption of the polymer molecules at the

interface, that consequently leads to reduction in surface tension. Furthermore, since the polymer under investigation is a non-polyelectrolyte polymer, the reduction in surface tension with NaCl could not have been due to the neutralization of surface charge of micelles by the NaCl added, which causes decrease in the repulsive forces among the ionic groups (hydrophilic chains). This behaviour is therefore unusual at least to our knowledge. Because non-polyelectrolyte polymers usually exhibit low surface activity with salt. In fact, it has been observed that in contrast to the polyelectrolyte polymers, the surface and interfacial activities of Zwitterionic polysoaps diminished by adding salt due to their anti-polyelectrolyte character [100]. However, hydrophobically modified PVA under investigation exhibits a contrasting behaviour of a typical non-polyelectrolyte polymers. The polymer surface tension decreases with NaCl concentration.

Figure 6.20 shows the effect of molecular weight on the surface tension of the hydrophobically modified polymer. The hydrophobically modified PVA of molecular weight of 100,000 is observed to have a slightly higher surface activity than that of modified PVA with 72,000. This behaviour is observed for all the polymer concentrations considered at 30° C.

The slight decrease in surface tension as polymer molecular weight increases from 72,000 to 100,000 could be attributed to the increase in adsorption of polymer molecules at water-air interface.

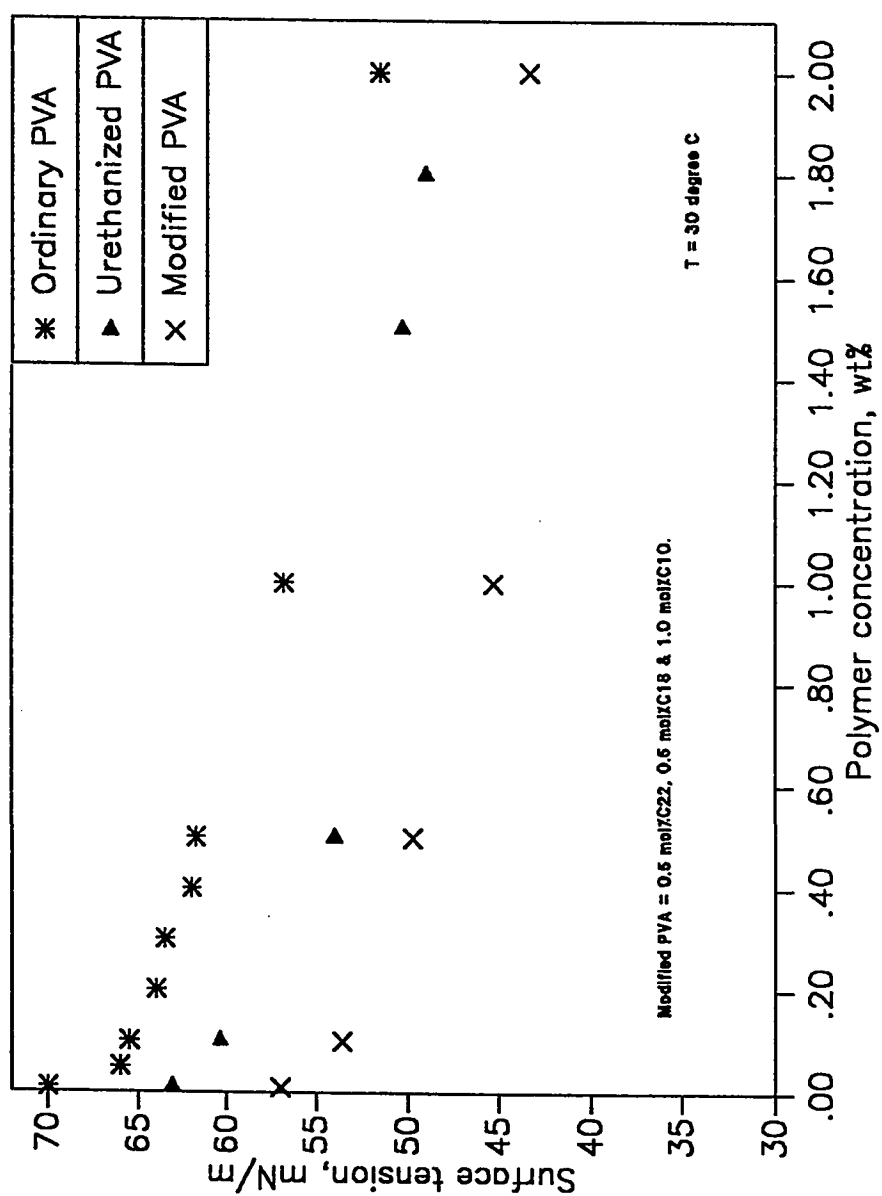


Figure 6.13: Plots of surface tension versus polymer wt% conc. for modified, urethanized & ordinary PVA with MW of 72,000.



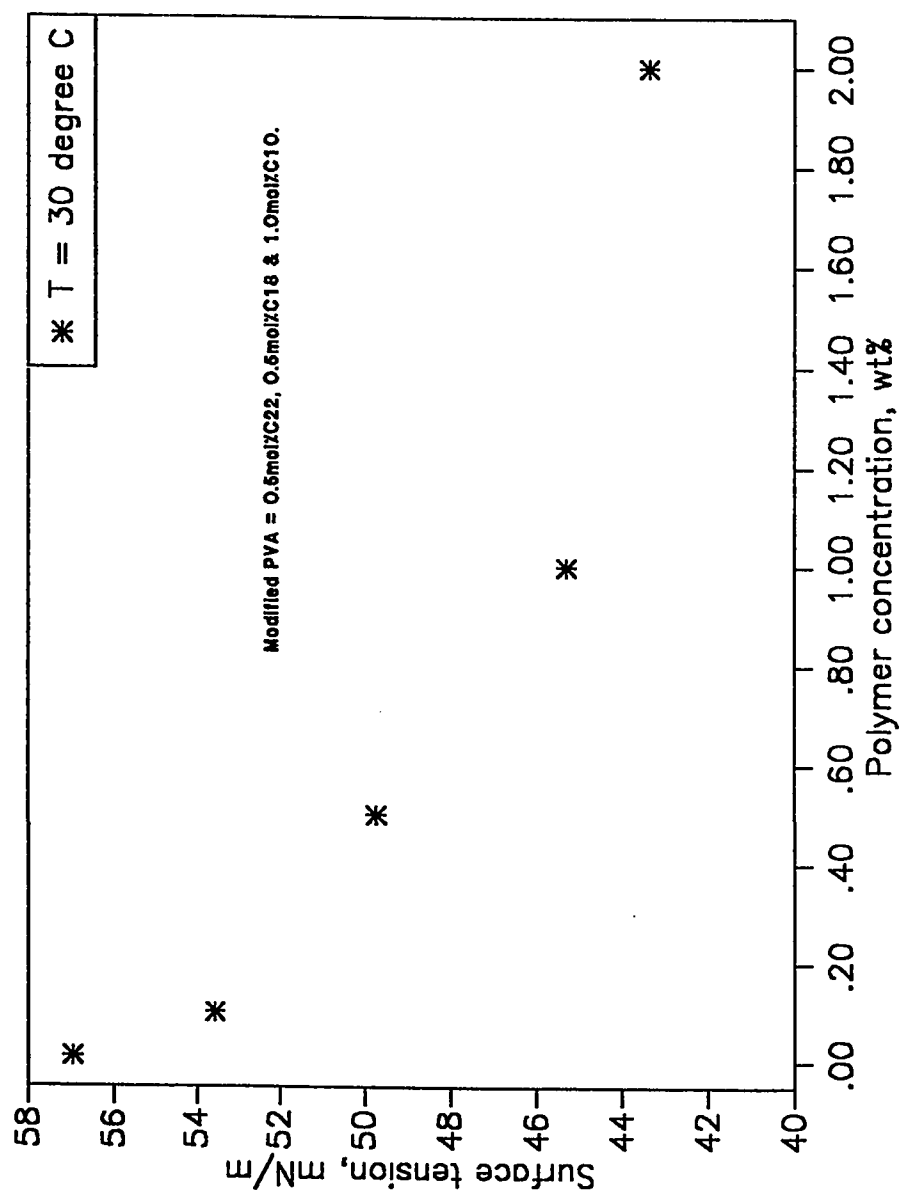


Figure 6.14 : Plot of surface tension versus polymer wt% concentration for modified PVA with molecular weight of 72,000.

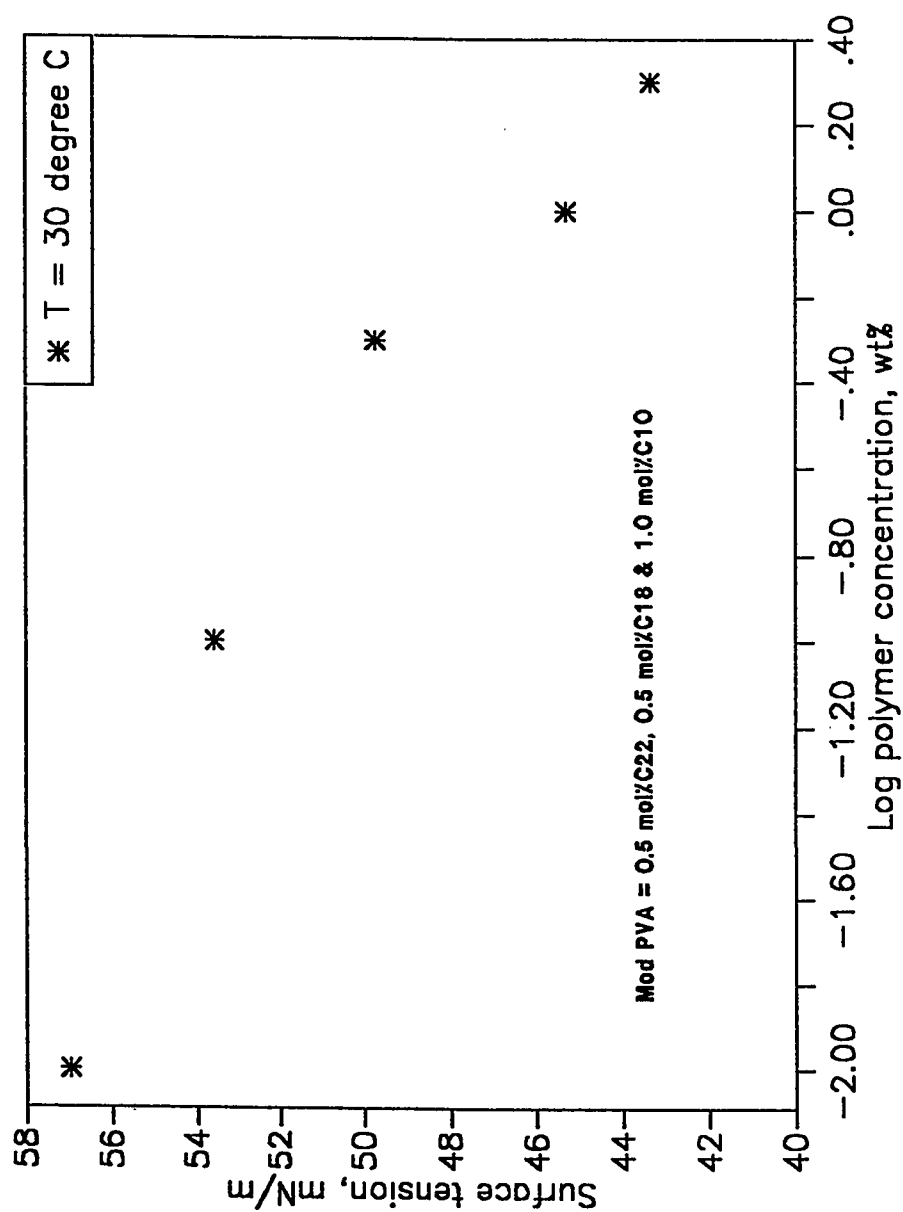


Figure 6.15 : Plot of surface tension versus Log polymer wt% concentration for modified PVA with molecular weight of 72,000.

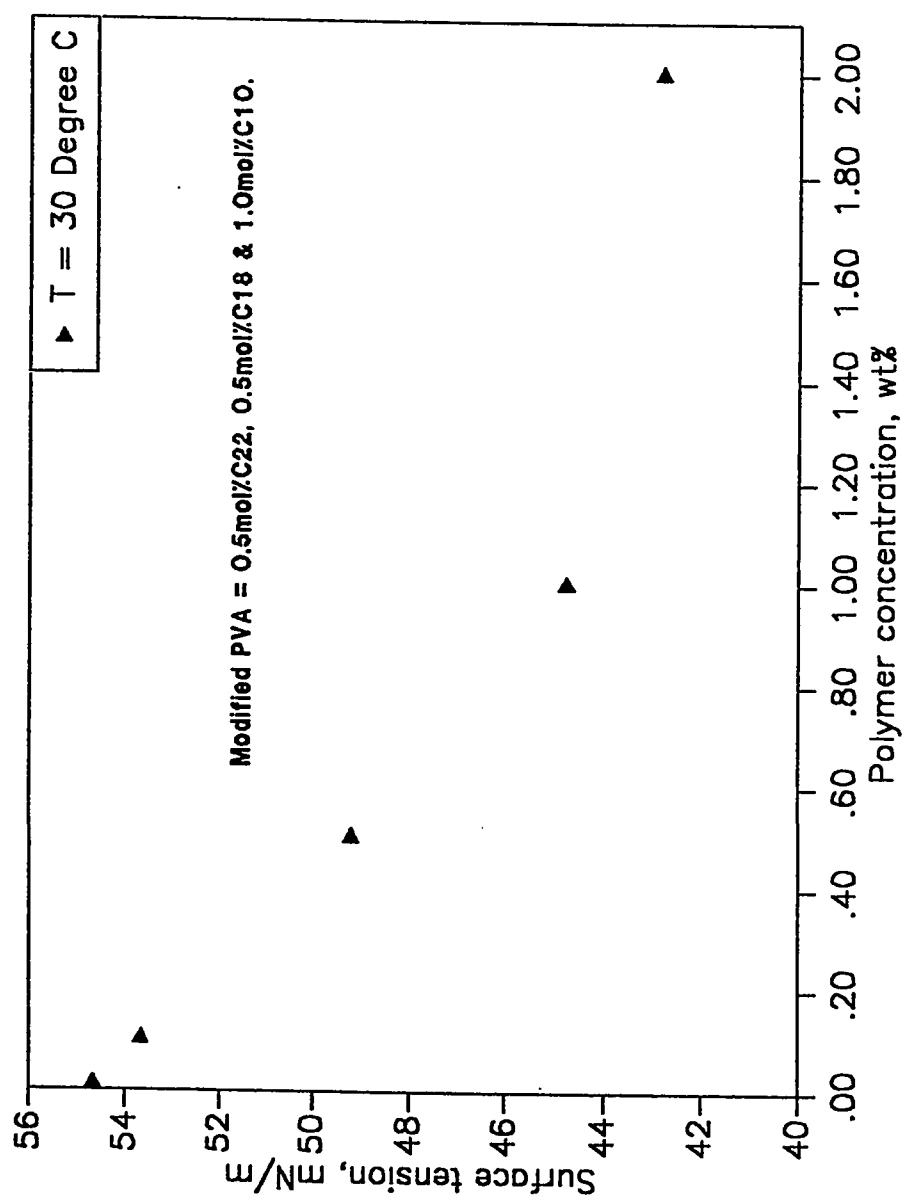


Figure 6.16 : Plot of surface tension versus polymer wt% concentration for modified PVA with molecular weight of 100,000.

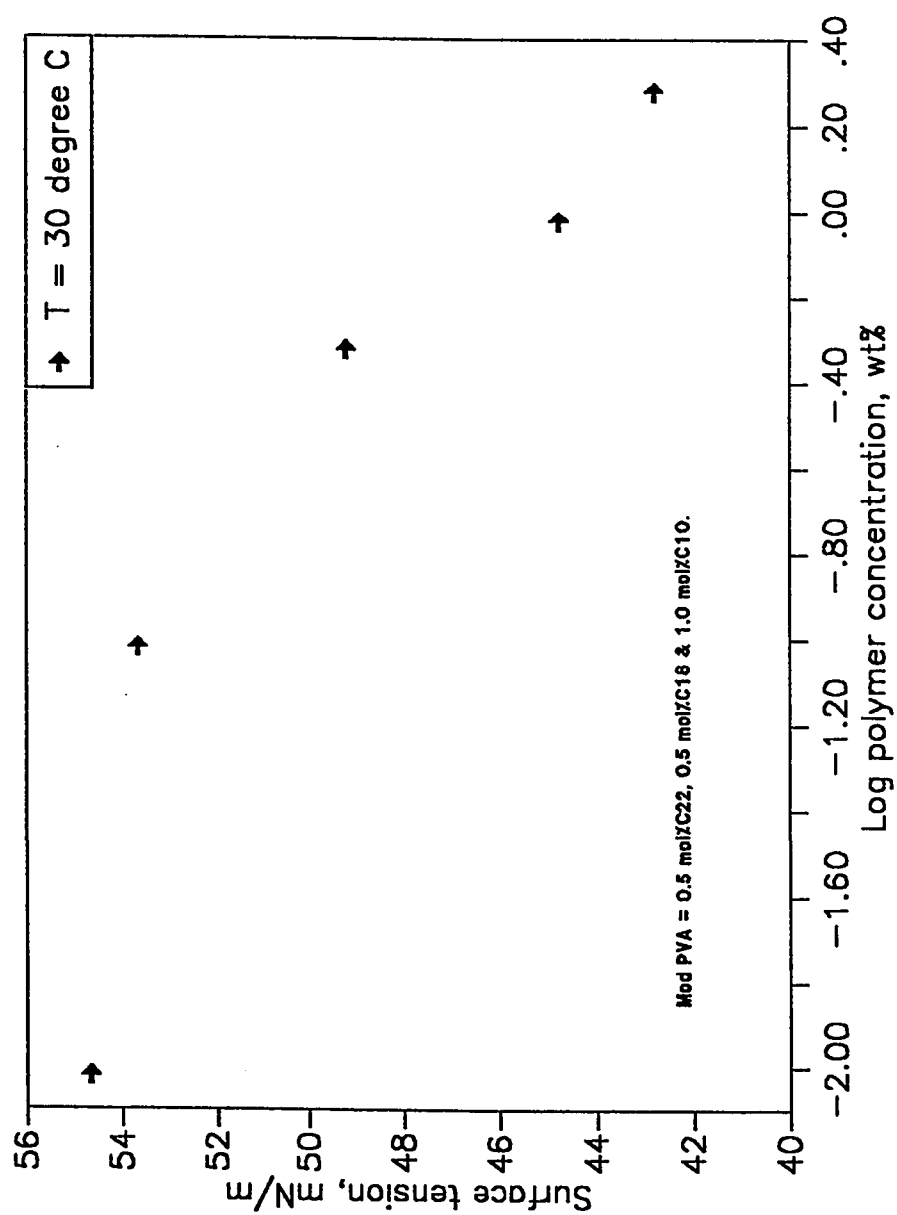


Figure 6.17 : Plot of Surface tension versus Log polymer wt% concentration for modified PVA with molecular weight of 100,000.

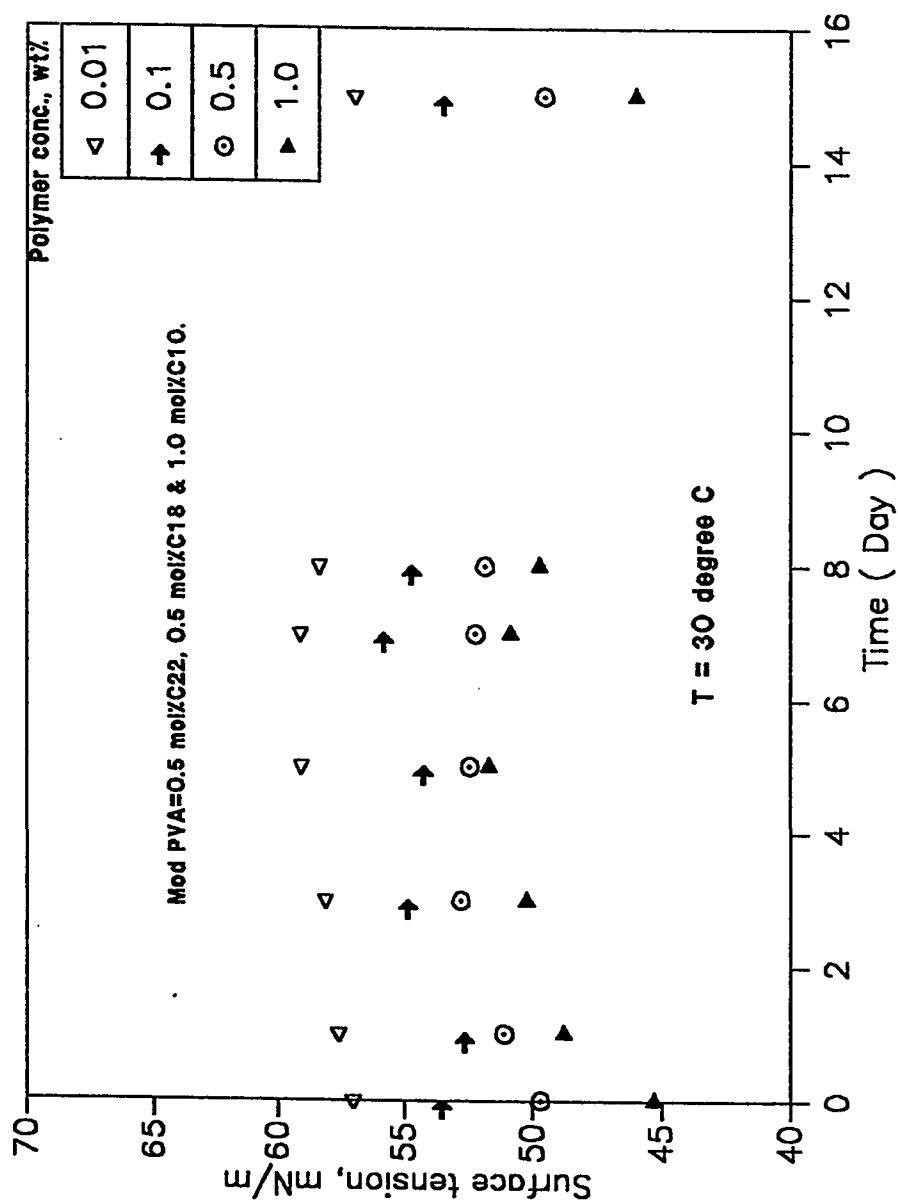


Figure 6.18 : Variations of surface tension—time relationship with polymer concentration for modified PVA of MW of 72,000.

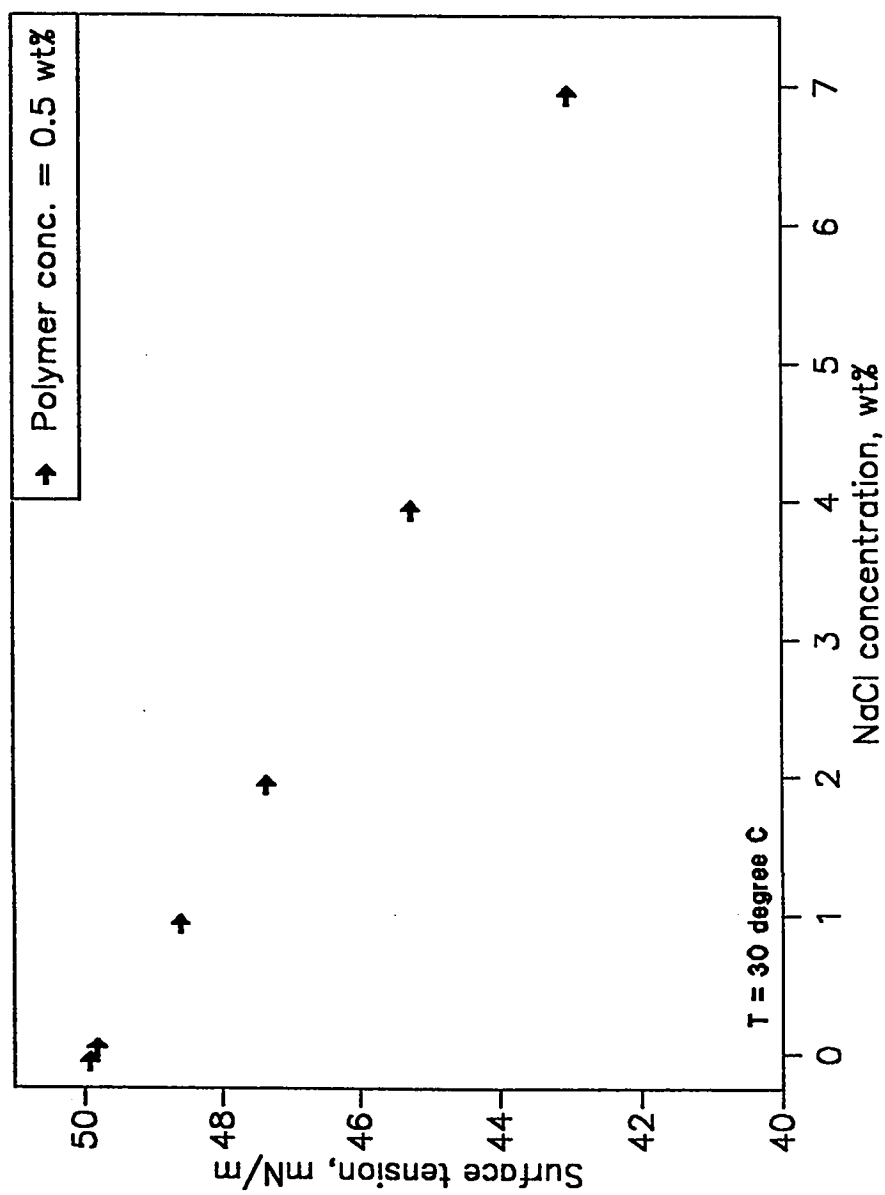


Figure 6.19 : Effect of NaCl on the surface tension of modified PVA ( 0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10) with MW of 72,000.

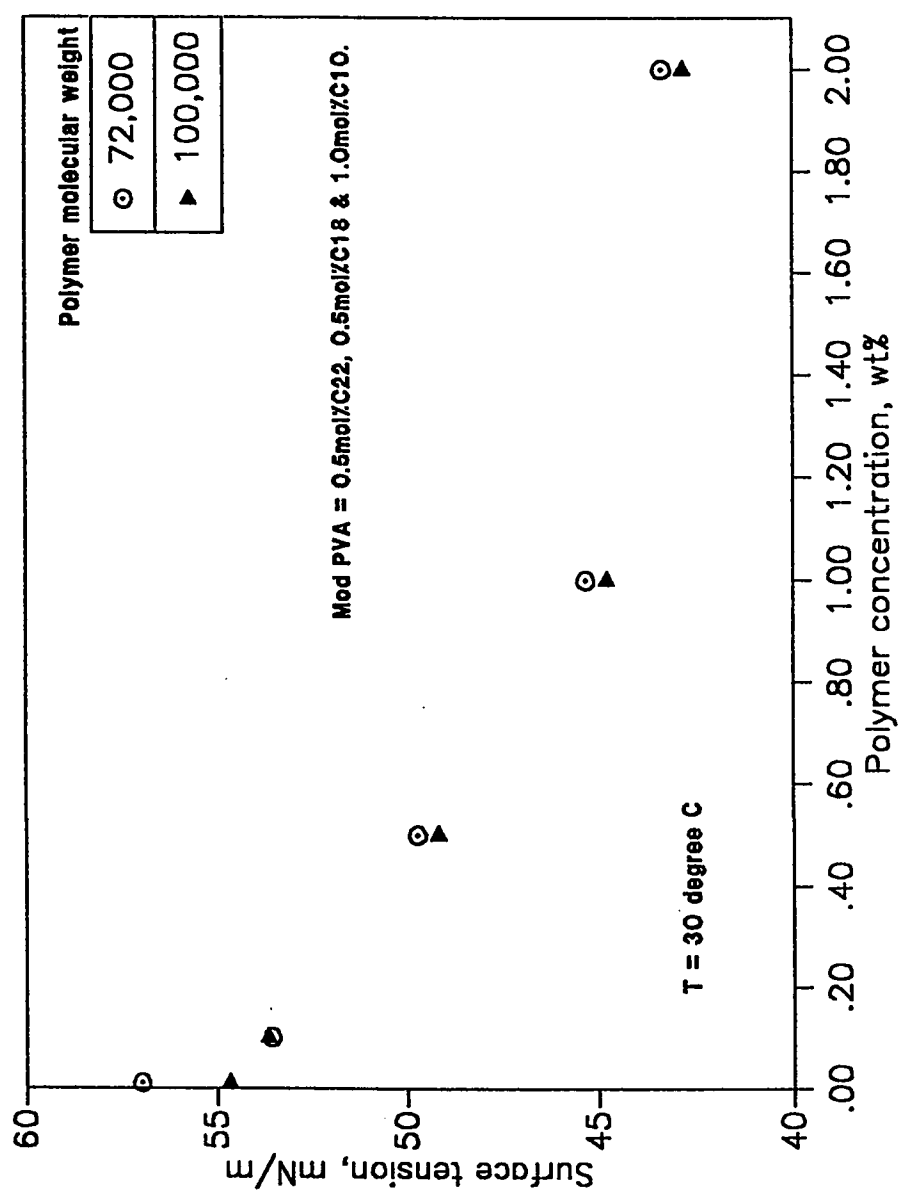


Figure 6.20 : Effect of polymer molecular weight on the surface tension—polymer conc. relationship for modified PVA at 30 degree C.

### 6.4.3 Interfacial tension Behaviour of Hydrophobically

#### Modified Polyvinyl alcohol ( PVA ).

The oil-water interfacial tensions (IFT) of the modified PVA were determined using the ring method. N-decane was used in this study as the oil phase. The detailed description of the procedure is given in chapter 3. The IFT of the aqueous solution/decane was measured for two polymer concentrations, i.e 0.5 wt% and 2.0 wt% at different NaCl concentrations ranging from 0-7.0 wt% and all the measurements were performed at 25° C. Attempts were also made to measure IFT for higher polymer concentrations, such as 5.0 wt% polymer concentration with different NaCl concentrations. Unfortunately, it was not possible due to the very high viscosity of the polymer solution. The results of the measurement and the interfacial tension behaviour obtained with respect to polymer concentration, NaCl concentration, polymer molecular weight, and the effect of modification are displayed in tables 6.18-6.20 and figures 6.21-6.23 for both polymers of molecular weight of 72,000 and 100,000.

As expected, the IFT decreases as the polymer concentration increases from 0.5 to 2.0 wt%. The same explanation for the decrease in surface tension with increasing polymer concentration observed in the previous section also holds here. The decrease in the IFT is due to the adsorption of the polymer molecules at the aqueous solution/decane interface. The increase in concentration of the polymer molecules at the interface, as the polymer concentration increases could be attributed to the amphiphilic structure of the polymer [45]. This trend is observed for the two polymers of molecular weight of 72,000 and 100,000 and for all the different polymer/NaCl solutions combinations considered.



Furthermore, a very interesting feature observed for the modified polymer is the decrease in IFT with increasing NaCl concentration. This behaviour is actually expected, since a similar one has been observed in the surface tension of the polymer as already discussed earlier in the previous section. IFT decreases with increasing NaCl concentration for both polymers of molecular weight 72,000 and 100,000. This behaviour is depicted in figures 6.21 and 6.22. This observation is actually very interesting as the polymer can be suited for petroleum reservoir with high salinities. The behaviour is however unusual, atleast for a nonionic polymer like the ones under consideration. Although, to our knowledge no work on IFT of hydrophobically modified polymers like the ones under investigation has been reported.

Furthermore, from the perspective of surface activity of nonionic polymer, non-polyelectrolyte polymers usually exhibit low surface activity with salt. Infact it has been reported that in contrast to the polyelectrolyte polymers, the surface activity of Zwitterionic polysoaps diminished by adding salt due to their anti-polyelectrolyte character [100]. However, the hydrophobically modified PVA under investigation exhibits a contrasting behaviour of a typical nonionic polymers.

Figure 6.23 shows the effects of NaCl, molecular weight and modification on the IFT of the modified PVA. As observed earlier, the IFT decreases with increasing NaCl concentration for urethanized PVA and the two modified PVA of molecular weight of 72,000 and 100,000. The modified PVA is also observed to exhibit higher interfacial activity than the unmodified PVA i.e urethanized PVA for the same polymer concentration of 2.0 wt%. This behaviour could be

attributed to the incorporation of hydrophobic groups on to the backbone of the polymer structure and also as result of the amphiphilic structure of the modified polymer which the unmodified do not possess. Similar behaviour was also observed by Chou. et al [5].

Furthermore, the hydrophobically modified PVA of molecular weight 100,000 is observed to have a slightly lower IFT than that of modified PVA with molecular weight of 72,000. This is observed for the same polymer concentration of 2.0 wt% and at 25° C.

The slight decrease in IFT as the molecular weight increases from 72,000 to 100,000 could be attributed to the enhancement of adsorption of polymer molecules at the interface, which probably leads to the increase in concentration of the polymer molecules at the air-aqueous solution interface. thus causes reduction in IFT.

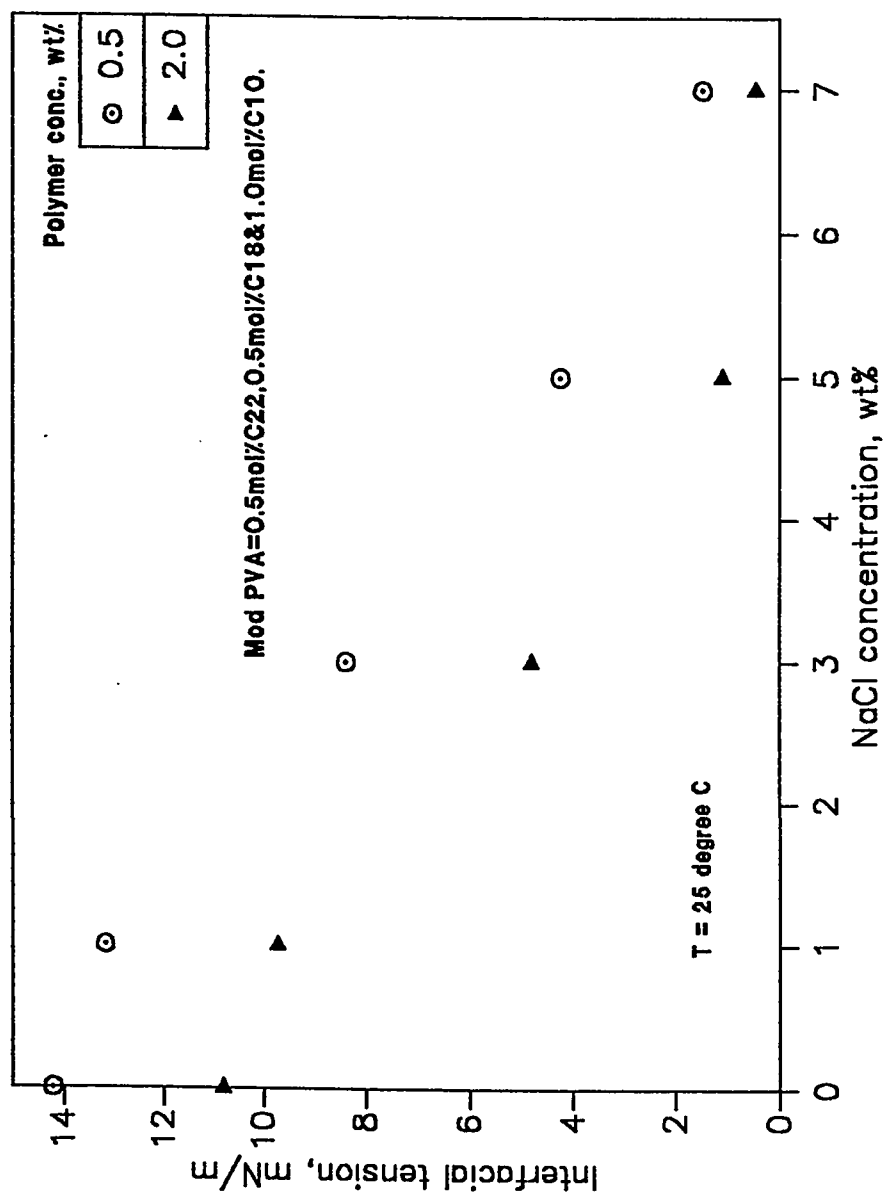


Figure 6.21 : Effect of NaCl conc. on the interfacial tension ( aqueous solution/decane ) of modified PVA with MW of 72,000.

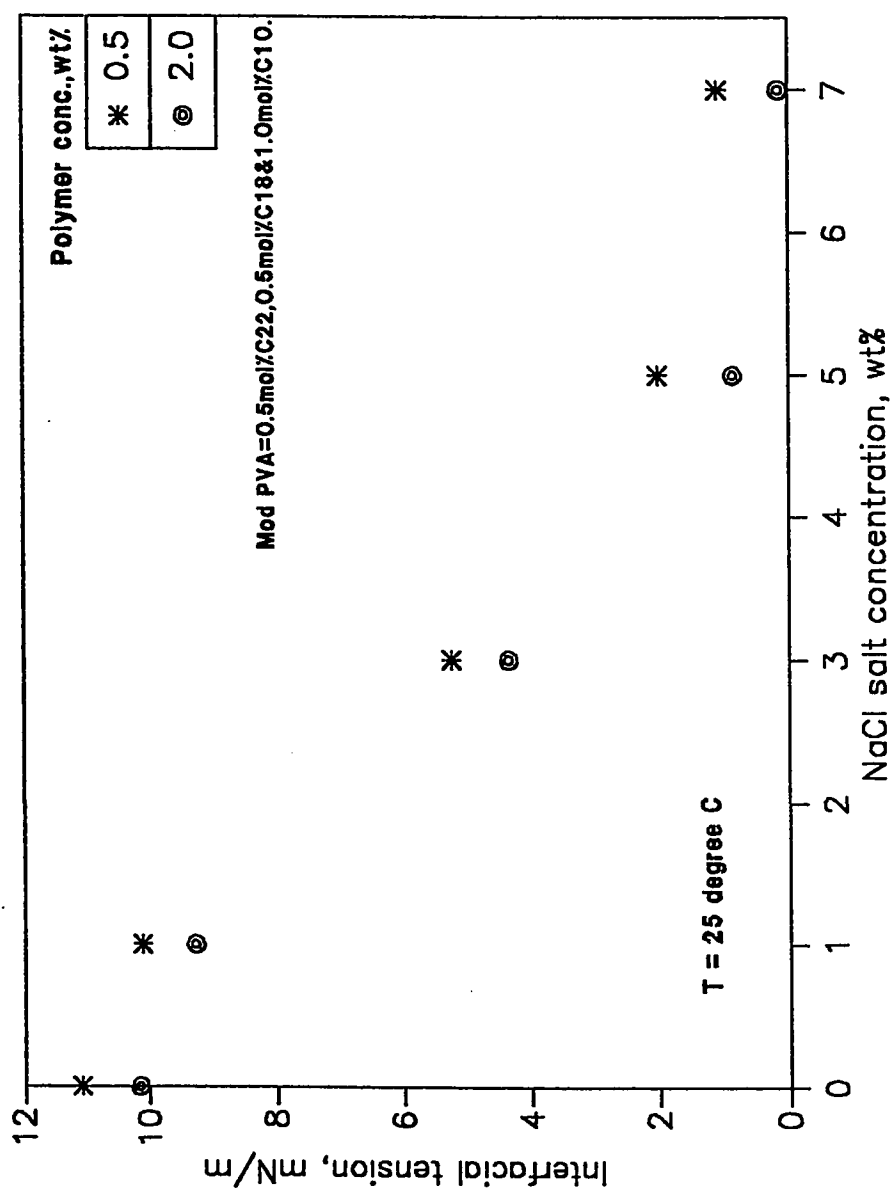


Figure 6.22 : Effect of NaCl conc. on the interfacial tension ( aqueous solution/decane ) of modified PVA with MW of 100,000.

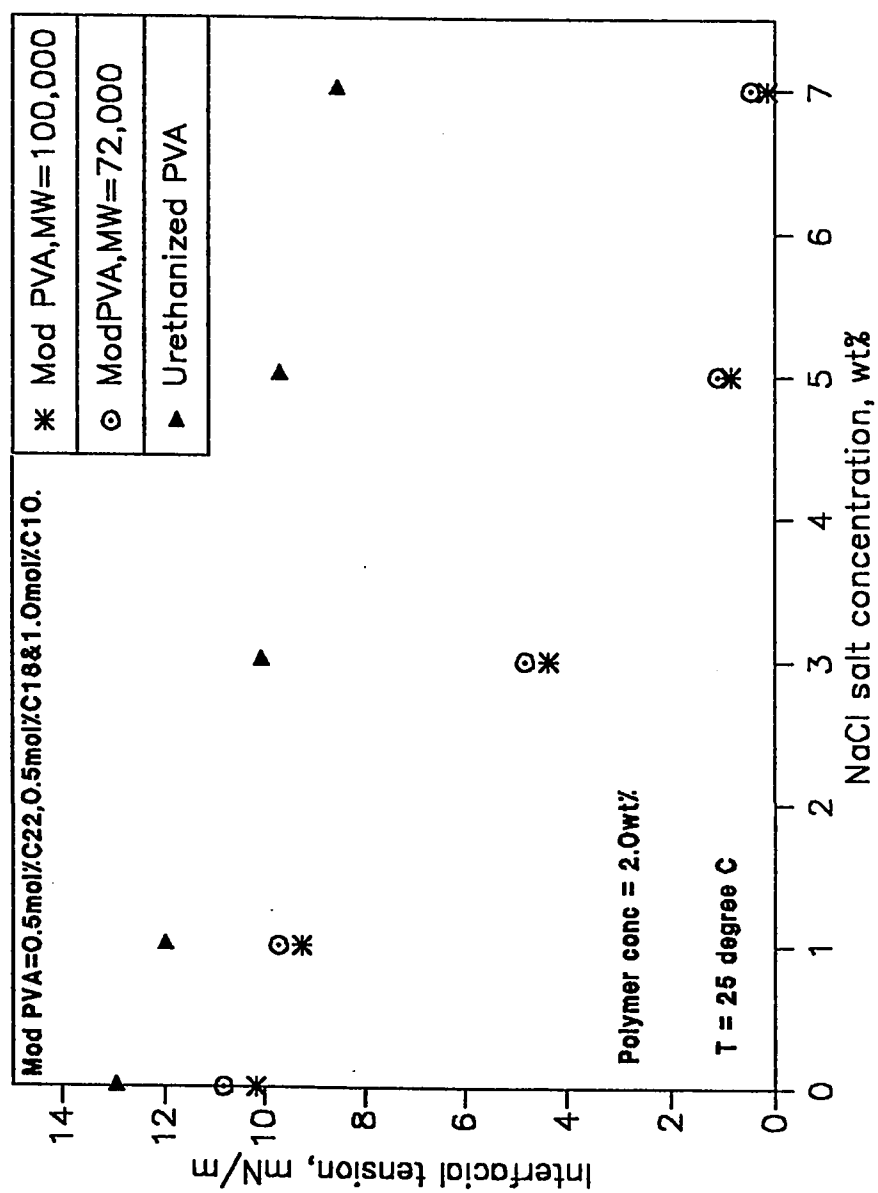


Figure 6.23 : Effects of NaCl conc., MW and modification on the interfacial tension ( aqueous solution/decane ) of modified PVA.

#### 6.4.4 Viscosity and Surface tension Behaviours of Other

##### Hydrophobically Modified Polyvinyl alcohol ( PVA ).

From the different combinations of the hydrophobically modified PVA displayed in table 6.1, the modified polymer with hydrophobic combination of 2.0 mol%C18 and 1.0 mol%C10 is also chosen for study in this work, because of its highest viscosity and low surface tension. The viscosity and surface tension behaviours of this polymer are studied briefly. It exhibits less surface activity than the earlier one, i.e 0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10, but highest viscosity.

Tables 6.21-6.23 and figures 6.24-6.27 display the results of viscosity and surface tension measurements and also the effects of polymer concentration, polymer modification, shear rate and NaCl on the viscosity and surface tension of the modified PVA with molecular weight of 72,000.

As displayed in figure 6.24, the modified PVA with hydrophobic groups combination of 2.0 mol%C18 & 1.0 mol%C10 is observed to exhibit greater viscosity enhancement than the one studied earlier, i.e 0.5 mol%C22, 0.5mol%C18 & 1.0 mol%C10. The viscosity of the former is observed to increase more drastic with increasing polymer concentration than the latter. This behaviour is probably due to the presence of more of the longer hydrophobic groups, i.e 2.0 mol%C18 in the modified PVA with hydrophobic combination of 2.0mol%C18 & 1.0mol%C10 than that of the other polymer studied earlier. The increase in the longer hydrophobic groups is probably causing more interchain hydrophobic interaction, which leads to a larger aggregate formation that results in large hydrodynamic radius and consequently causes the increase in viscosity.

Figures 6.24 and 6.25 also show the effect of polymer concentration on the viscosity of the modified PVA, i.e 2.0 mol%C18 & 1.0 mol%C10. As expected the viscosity of the polymer increases with increasing polymer concentration for all the shear rates considered. The same explanation for the increase in viscosity with polymer concentration observed for the polymer with hydrophobic combination of 0.5 mol%C22, 0.5 mol%C18 and 1.0 mol%C10 studied earlier also holds for this case.

Figure 6.25 displays the effect of shear rate on the viscosity of the polymer. An almost constant viscosity is observed at high shear rate for all the polymer concentrations considered. However, at low shear rate, a typical shear thinning appears. Similar behaviour is also observed for the modified PVA studied previously and thus same explanation for the behaviour can be given for this case as well.

Figures 6.25 and 6.26 depict the effect of NaCl salt on the viscosity of the polymer. A similar behaviour observed for the previous polymer is also observed for this polymer. A maximum viscosity is observed at about 1.0 wt% NaCl concentration. From this NaCl concentration, i.e 1 wt%, the viscosity decreases up to about 3.0 wt% NaCl concentration. Above 3.0 wt% viscosity increases sharply up to the last point.

This behaviour is actually expected, since the modified polymer is a non-polyelectrolyte, as such there are no charges to shield the electrostatic repulsion forces, which in turn could have leads to reduction in viscosity. Addition of NaCl is probably promoting more interchain hydrophobic interaction among hydrophobic groups in the polymer structure.

Figure 6.27 shows the effect of polymer concentration, modification and NaCl salt on the surface tension of the modified PVA with hydrophobic groups combination of 2.0 mol%C18 & 1.0mol%C10. As mentioned earlier, the modified PVA with combination of hydrophobic groups of 0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10, exhibits a greater surface activity than the one with 2.0 mol%C18 & 1.0 mol%C10. As shown in figure 6.27, the surface tension of the former is lower and decreases more drastic with increasing polymer concentration than that of the latter. This behaviour could be attributed to the presence of less of the longer hydrophobic groups in the modified polymer with hydrophobic groups combination of 0.5 mol%C22, 0.5 mol%C18 & 1.0 mol%C10 than the other polymer under investigation.

The surface tension of the polymer also decreases with increasing polymer concentration and NaCl concentration. This behaviour is also observed for the previous polymer already studied and thus the same explanation given for the behaviour of that polymer can also be given for the one under investigation.

Furthermore, table 6.1 and figures 6.28 and 6.29 display the effect of the ratio of average number of  $\text{CH}_2$  to the number of sidechain of a particular hydrophobic combination on solution viscosity and surface tension of some of the modified PVA displayed in table 6.1. As shown in figures 6.28 and 6.29, a decrease in viscosity and surface tension is observed with increasing the ratio, for the same total number of hydrophobic groups attached. For this case, the total number of hydrophobic groups considered are 3.0 mol% and 4.0 mol% as shown in figures 6.28 and 6.29 respectively; and these numbers are the same for each point shown in the figures. The decrease in viscosity could be attributed to



the intramolecular interactions of the hydrophobic groups which is probably predominant as the ratio of the average number of  $\text{CH}_2$  to the number of sidechain increases. This leads to the formation of compact micellar structure with small hydrodynamic volume, thus causes the reduction in solution viscosity. Surface tension is falling probably as a result of increase tendency of hydrophobic groups to adsorp more at the air-aqueous solution interface as the ratio is increased.

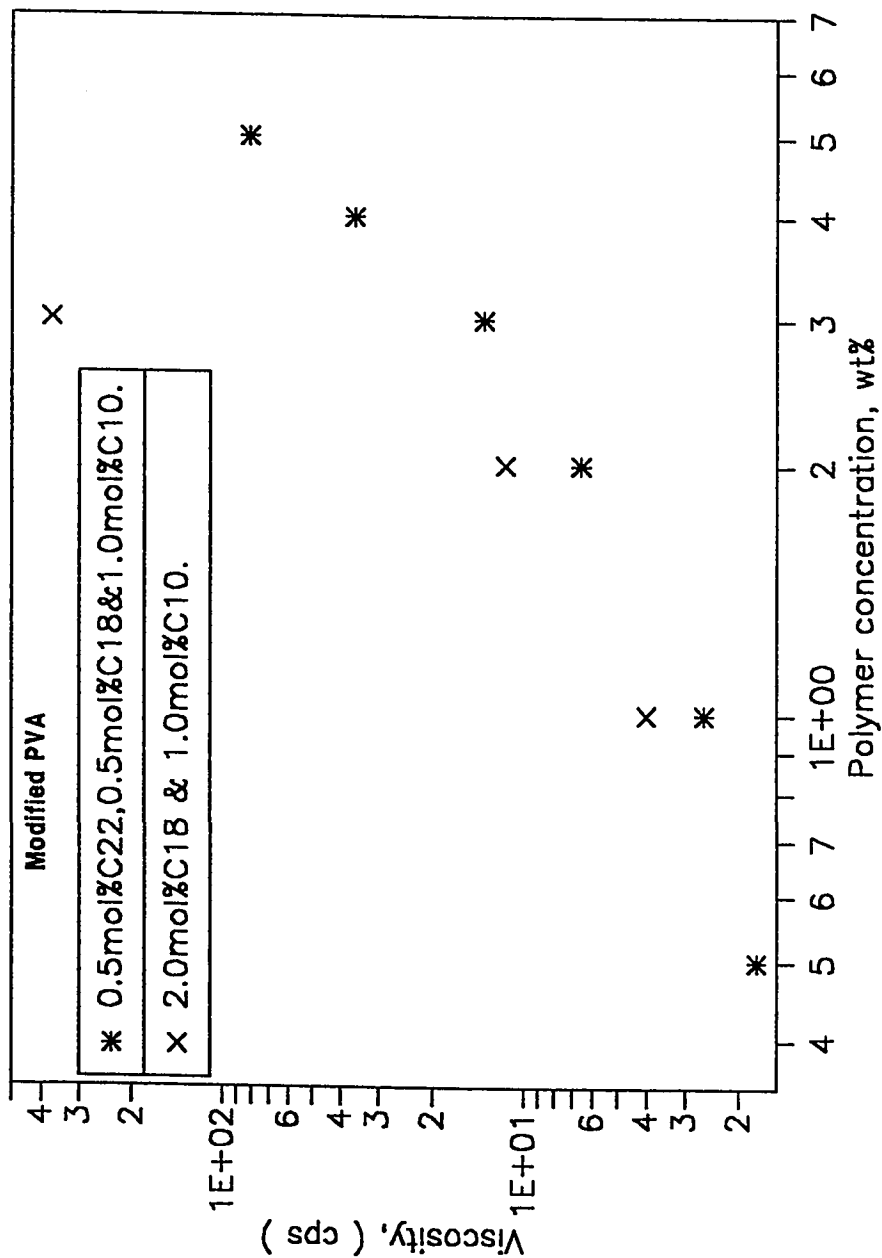


Figure 6.24 : Effects of polymer concentration and modification on the viscosity of modified PVA with MW of 72,000 at 30 degree C.

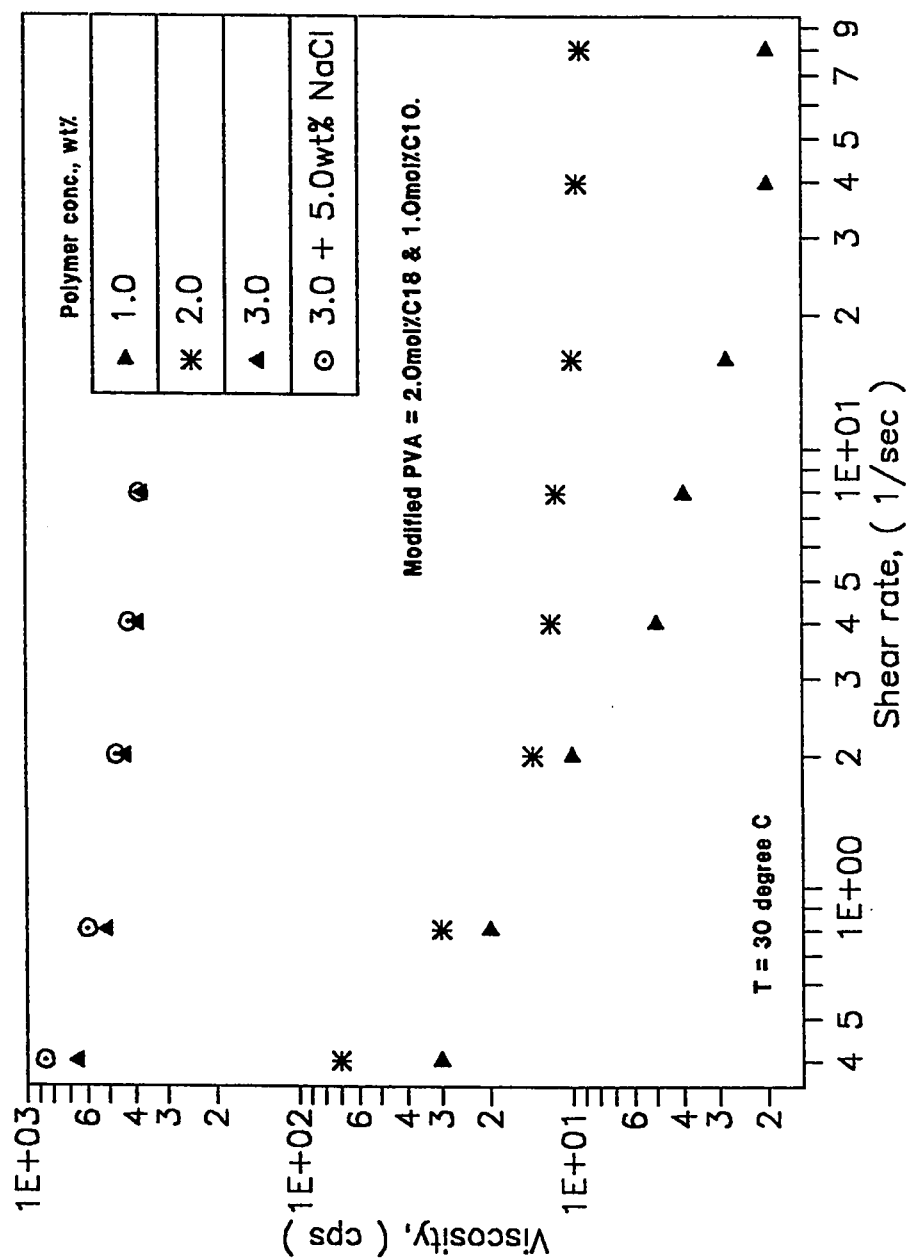


Figure 6.25: Variations of viscosity—shear rate relationship with polymer and NaCl concentrations for modified PVA of MW of 72,000.

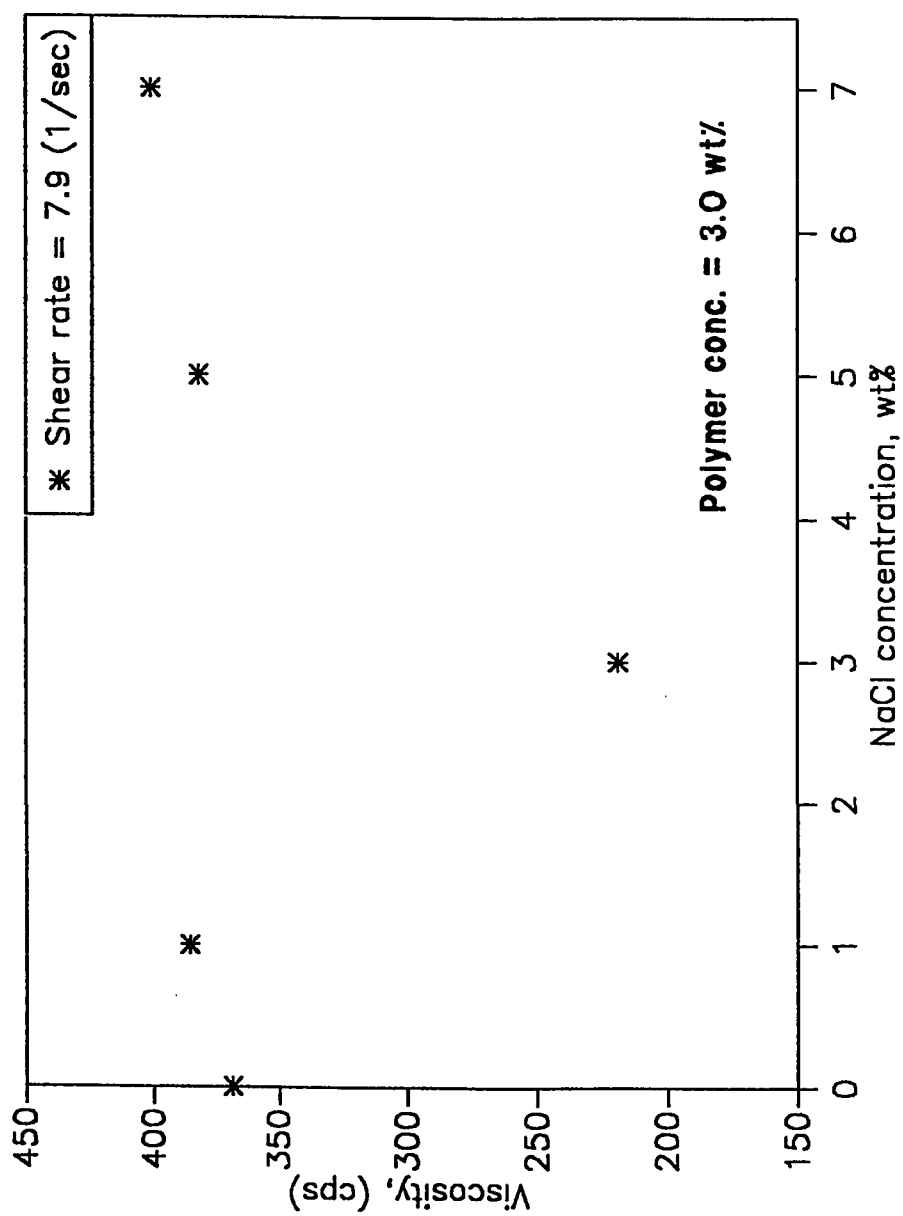


Figure 6.26 : Effect of NaCl conc. on the Viscosity of modified PVA (2.0mol% C18 & 1.0mol% C10.) with MW of 72,000 at 30 degree C.

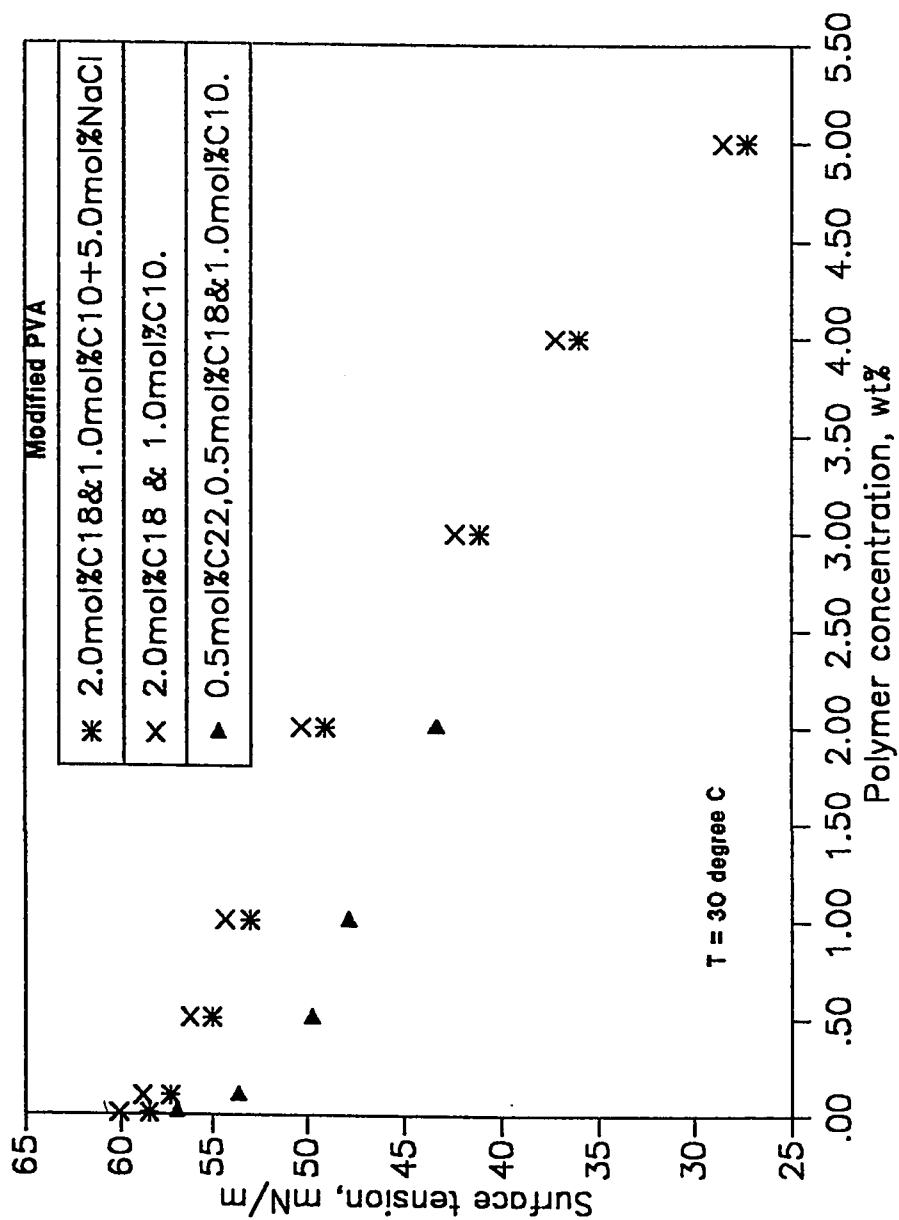


Figure 6.27 : Effects of polymer concentration, modification and NaCl on the surface tension of modified PVA with MW of 72,000.

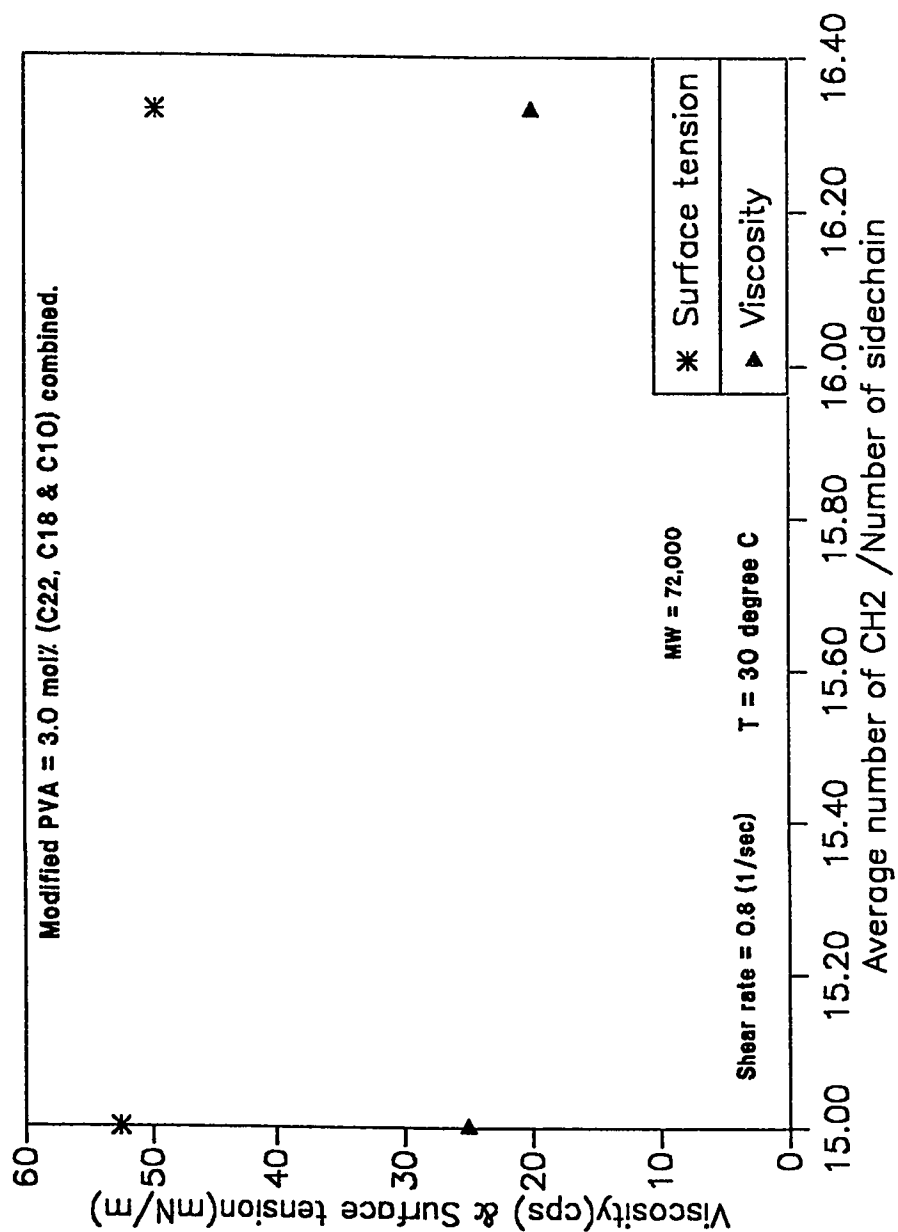


Figure 6.28 : Effect of the ratio of Average No. of CH<sub>2</sub> to No. of sidechain on viscosity and surface tension of modified PVA.

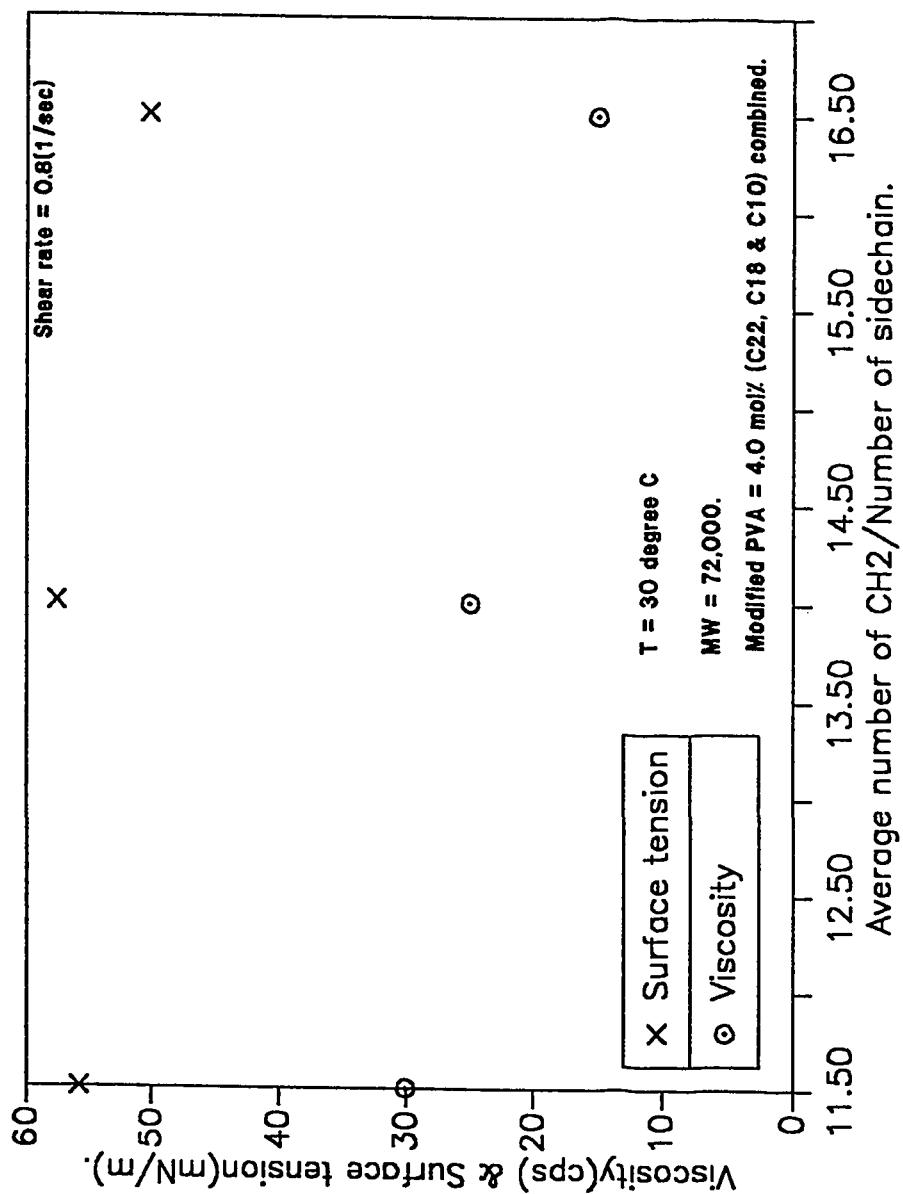


Figure 6.29 : Effect of the ratio of Average No. of CH<sub>2</sub> to No. of sidechain on viscosity and surface tension of modified PVA.

## 6.5 DISCUSSION AND CONCLUSIONS.

In general, the viscosity of the hydrophobically modified polyvinyl alcohol (PVA) is high at moderate polymer concentrations. For this modified polymer, the hydrophobic associations are predominantly intermolecular in nature, since intramolecular interactions would have resulted in a low rather than a high solution viscosity.

Furthermore, the hydrophobically modified PVA exhibits a relatively high salt tolerance in the range of 0-7.0 wt% NaCl concentration. Thus the polymers could be suited for a petroleum reservoir with relatively high salinities.

Hydrophobically modified PVA also exhibits good surface and interfacial activities, including low surface and interfacial tensions, (IFT). Although for the polymer concentrations considered in this work, the surface tension and IFT obtained are only moderate compared to conventional surfactants which exhibit ultimate surface tension and IFT values in the range of 20-40 mN/m and  $10^{-3}$  mN/m respectively. The ultimate IFT value obtained for this polymer is in the range of  $10^{-1}$  mN/m. No CMC, or break point resembling CMC is observed for the hydrophobically modified PVA.

Generally, the viscosity-shear rate relationship for the polymers exhibit a nearly constant viscosity behaviour at high shear rate and a shear thinning behaviour at low shear rate. The shear thinning characteristics of the polymers would actually be an advantage in polymer flooding. Because in the high shear region around the injection well bore, the effective viscosity of the injected polymers would be relatively low, thus requiring low power to move. However,



it would increase with decreasing shear as the polymer solution penetrates more deeply into the formation.

Increasing the polymer concentration causes increase in the polymer viscosity. Interchain association of hydrophobic groups in the polymer is enhanced as the polymer concentration increases. The hydrophobically modified PVA also exhibits viscosity reduction with increasing temperature

The relative invariance of viscosity to changes in salt concentration above 3.0 wt% of NaCl concentration is one of the attractive feature of these associative polymers. In this study, adding NaCl is probably promoting intermolecular hydrophobic association among hydrophobic groups in the polymer structures.

Incorporation of hydrophobic groups on to the backbone of the modified polymer gives the polymer a greater thickening ability. This indicates the occurrence of hydrophobic association among the hydrophobic groups in the polymer structure.

As expected, the polymers exhibit a greater viscosity enhancement and higher surface and interfacial activities, for higher molecular weight than for lower molecular weight polymer.

A slight reduction in viscosity is displayed by the polymers with ageing. Evidence of instability in the polymer structure is indicated. The stability can be improved by using other links which are more stable than the ester linkage.

The hydrophobically modified polymers with only C18 hydrophobic group

exhibit cloudiness and insolubility in aqueous solution, while those with both C18 and C10 hydrophobic groups exhibit complete solubility in water. This then indicates balance between hydrophobic and hydrophilic forces is necessary for polymer solubility.

Furthermore, it can be concluded from this study, that the larger the amount of long hydrophobic groups in the polymer structure, the greater is the viscosity and the lower is the surface activity of the polymer. In addition, increasing the ratio of average number of  $\text{CH}_2$  to the number of sidechain leads to decrease in viscosity and surface tension.

Moreover, hydrophobically modified PVA exhibits a decrease in surface tension and IFT with increasing polymer concentration. Evidence of more adsorption of the polymer molecules at the water-oil interface is indicated. The surface tension is also time dependent.

Incorporation of hydrophobic moieties on to the backbone of the original polymer (PVA) increases its ability to exhibit high surface and interfacial activities. This behaviour is as a result of the amphiphilic structure of the polymer.

Conclusively, adding NaCl to the polymer solutions increases its surface and interfacial activities. This behaviour is unusual, atleast for a non-polyelectrolyte polymers like the ones under consideration, which are usually known to diminish in surface and interfacial tensions when salt is added. This observation is another attractive feature of these polymers, as the polymers can be suited for a petroleum reservoir with high salinities.

## CHAPTER 7

### CONCLUSIONS AND RECOMMENDATIONS.

#### 7.1 SUMMARY AND GENERAL CONCLUSIONS

In this work, attempts have been made to design associative sidechain polymers that can simultaneously provide high viscosity for mobility control and ultralow interfacial tension for enhanced microscopic displacement efficiency in enhanced oil recovery operations. In order to achieve this objective, three classes of amphiphilic sidechain polymer that include, cyclopolymer of diallyl quaternary ammonium salt, copolymers of maleic anhydride/1-alkene and hydrophobically modified polyvinylalcohol (PVA) have been synthesized or modified. The rheological behaviour and surface and interfacial activities of these polymers have also been studied with respect to the polymers concentration, temperature, salinity, shear rate, polymers molecular weight and time.

From this study, one of the polymers obtained, i.e hydrophobically modified PVA, gives high viscosity that can be compared to what is usually required in enhanced oil recovery applications, although at high polymer concentrations. Large enhancement in the interfacial activity of the polymers was obtained, although the ultimate interfacial tension given by the polymers studied in this work, does not fulfill the requirement of enhanced oil recovery operations. However, it seems possible that improved or better polymers could be designed to simultaneously provide high solution viscosity and ultralow interfacial tension (IFT) for use in enhanced oil recovery operations.

The viscosity, surface and interfacial tensions of the copolymers of maleic anhydride/1-alkene and the cyclopolymer are found to be low. It can thus be deduced that the larger the numbers of hydrophobic groups in the polymer structure, the smaller is the viscosity and the lower are the surface and interfacial tensions. For these polymers, the hydrophobic interactions are predominantly intramolecular in nature, which probably promote micellization. In addition, it can also be deduced that the longer the hydrophobic groups in the polymer structure, but not in large numbers, the greater is the viscosity. This is evidenced from the value of viscosity obtained for the hydrophobically modified PVA, which is found relatively high at moderate polymer concentration. For this hydrophobically modified polymer, the hydrophobic interactions are predominantly intermolecular in nature, that probably promote association. Moreover, increasing the ratio of average number of  $\text{CH}_2$  to the number of sidechain leads to reduction in viscosity and surface tension of modified polyvinylalcohol (PVA). All the above deductions could be seen and could be self-explained in the diagram shown in figure 6.30.

Incorporating hydrophobic groups on to the backbone of the original PVA increases the polymer's ability to exhibit high surface and interfacial activities; and also gives the polymer greater thickening ability as evidence from the values of viscosity, surface and interfacial tensions obtained for the hydrophobically modified PVA. The enhanced thickening ability is due to the interchain association of the hydrophobic groups. The enhanced surface and interfacial activities are due to the amphiphilic structure of the hydrophobically modified polymer. Moreover, balance between hydrophobic and hydrophilic

forces on polymer backbone is necessary for polymer solubility.

The cyclopolymer of diallyl quaternary ammonium chloride and the copolymers of maleic anhydride/1-alkene in aqueous solution exhibit low salt tolerance, typical of polyelectrolytes, in the range of 0-1.0 wt% NaCl concentration. However, a relatively high salt tolerance, typical of nonionic polymers is exhibited by the hydrophobically modified PVA, in the range of 0-7.0 wt% NaCl concentration.

Good surface and interfacial activities, including low surface and interfacial tensions are exhibited by the three classes of polymer considered in this work. Moreover, surface and interfacial tensions decrease with increasing polymer concentrations for all the polymers considered. Surface tension of 45mN/m at CMC of 0.29 wt% is obtained for the copolymer of maleic anhydride/1-dodecene and 42.7mN/m at CMC of 0.419 wt% is obtained for the copolymer of maleic anhydride/1-hexadecene. No CMC or a break point resembling CMC is exhibited by the hydrophobically modified PVA and cyclopolymer of diallyl quaternary ammonium chloride. The ultimate interfacial tension values obtained for the copolymers and hydrophobically modified PVA are in the range of 1.0 mN/m and  $10^{-1}$  mN/m respectively. These values are however, only moderate compared to conventional surfactants used in enhanced oil recovery applications, which exhibit ultimate interfacial tension in the range of  $10^{-3}$  mN/m.

The viscosity of the hydrophobically modified PVA is relatively invariant with NaCl concentrations above 3.0 wt% NaCl concentration. Similar

behaviour is observed for the copolymers of maleic anhydride/1-alkene. Furthermore, adding NaCl to the polymer solution of the modified PVA and copolymers increases their surface and interfacial activities. The copolymers also exhibit a decrease in surface tension with time at high polymer concentration and invariance with time at low polymer concentration. The hydrophobically modified PVA with high molecular weight, i.e 100,000 exhibits a greater thickening ability and higher surface and interfacial activities than the one with low molecular weight, i.e 72,000. A slight reduction in viscosity is also exhibited by the modified polymer with time (ageing).

Generally, for the three classes of polymers considered in this work the viscosity-shear rate relationship exhibits a nearly constant viscosity at high shear rates and a typical shear thinning behaviour at low shear rates. In addition, increasing polymer concentration leads to an increase in the polymers solution viscosity. Moreover, the polymers exhibit a reduction in solution viscosity with increasing temperature.

## 7.2 RECOMMENDATIONS.

In order to reveal the conditions at which middle phase microemulsions and ultralow interfacial tensions are achieved, the study of the phase behaviour of all the three classes of polymer considered in this work should be carried out.

Furthermore, in order to test the data generated in this study, a molecular model that can predict the interfacial behaviour of the polymers in aqueous solutions should be developed

The viscosity of the hydrophobically modified PVA is found to decrease with ageing. This could be attributed to the hydrolysis of the ester group which links the structure. The stability of this polymer structure should therefore be improved by using other links, such as amide or ether linkage that are more stable than the ester linkage used in this work.

The study of adsorption and injectability of the polymers considered in this work, should also be carried out on sandstone and carbonate rock samples, in order to find out whether the polymers are suitable for real enhanced oil recovery operations.

Peculiar solution viscosity behaviour of the hydrophobically modified PVA such as the effect of NaCl salt on solution viscosity should be studied.

By applying the conclusions arrived at in this work, better polymers that can provide the solution properties required in enhanced oil recovery operations could be designed.

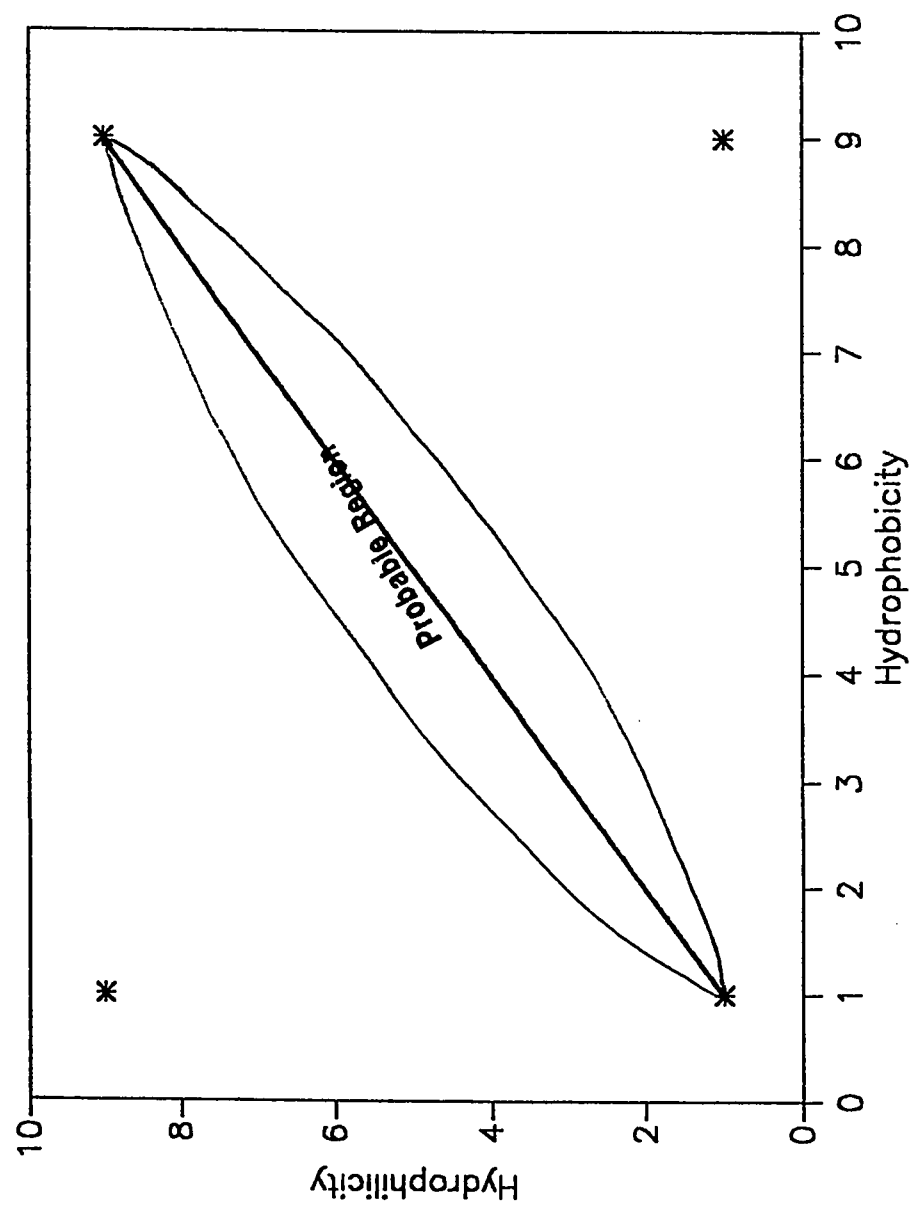


Figure 6.30: Effect of Hydrophobicity and Hydrophilicity on the solution properties of all the polymers designed in this work.



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## **APPENDIX A**

**Table 5.2: The Viscosity-Shear rate-Temperature Data  
for Copolymer of Maleic anhydride/1-dodecene, measured  
for Polymer concentration of 6.7 wt%**

Speed (RPM)	Shear rate ( 1/sec )	Viscosity at 25 degree C ( cps )	Viscosity at 30 degree C ( cps )	Viscosity at 50 degree C ( cps )	Viscosity at 90 degree C ( cps )
30.0	36.7	1.7	1.5	1.0	0.8
60.0	73.4	1.6	1.4	1.0	0.8

**Table 5.3: The Viscosity-Shear rate-Temperature Data**  
**for Copolymer of Maleic anhydride/1-dodecene, measured**  
**for Polymer concentration of of 2.7 wt%.**

Speed (RPM)	Shear rate ( 1/sec )	Viscosity at 25 degree C ( cps )	Viscosity at 30 degree C ( cps )	Viscosity at 50 degree C ( cps )	Viscosity at 90 degree C ( cps )
30.0	36.7	1.3	1.2	0.8	0.5
60.0	73.4	1.3	1.2	0.8	0.5



**Table 5.4: The Viscosity-Shear rate-Temperature Data**  
**for Copolymer of Maleic anhydride/1-hexadecene. measured**  
**for polymer concentration of 8.1 wt%.**

Speed (RPM)	Shear rate ( 1/sec )	Viscosity at 25 degree C ( cps )	Viscosity at 30 degree C ( cps )	Viscosity at 50 degree C ( cps )	Viscosity at 90 degree C ( cps )
30.0	36.7	1.8	1.5	1.1	0.8
60.0	73.4	1.8	1.5	1.0	0.8

**Table 5.5: The Viscosity-Shear rate-Temperature Data**  
**for Copolymer Maleic anhydride/1-hexadecene, measured**  
**for Polymer concentration of 3.2 wt%.**

Speed (RPM)	Shear rate ( 1/sec )	Viscosity at 25 degree C ( cps )	Viscosity at 30 degree C ( cps )	Viscosity at 50 degree C ( cps )	Viscosity at 90 degree C ( cps )
30.0	36.7	1.2	1.1	0.8	0.5
60.0	73.4	1.2	1.0	0.8	0.5

Table 5.6: The Viscosity-NaCl Concentration Data for  
Copolymers of Maleic anhydride/1-dodecene and Maleic  
anhydride/1-hexadecene, measured at 30 degree C and at Shear  
rate of 73.4 (1/sec) for polymer concentration of 2.7 wt%.

NaCl conc (wt%)	Viscosity of Poly I (cps)	Viscosity of Poly II (cps)
0.0	1.21	1.60
0.1	1.60	2.01
0.3	1.60	2.40
0.5	1.60	2.40
0.75	1.60	***
1.00	2.01	***

where

Poly I = Copolymer of maleic anhydride/1-dodecene

Poly II = Copolymer of maleic anhydride/1-hexadecene.

\*\*\* = Inaccurate (Less than 5% of the full range in use).

**Table 5.7: The Surface tension-Polymer concentration Data for  
Copolymer of Maleic anhydride/1-dodecene Measured at  
30 degrees C .**

Polymer conc. ( wt% )	Log Polymer conc. (wt%)	Surface tension (mN/m) at day 1	S.T ( mN/m ) after 96 days
0.0098	-2.009	67.24	70.19
0.0196	-1.708	64.13	65.44
0.0391	-1.408	57.59	58.51
0.0782	-1.107	60.61	52.25
0.1563	-0.806	52.65	49.59
0.3125	-0.505	48.97	45.50
0.625	-0.204	48.00	43.50
1.25	0.097	47.21	43.25
2.5	0.398	45.00	42.79
5.0	0.699	44.25	42.68

**Table 5.8: The Surface tension-Polymer concentration Data for  
Copolymer of Maleic anhydride/1-hexadecene Measured at  
30 degrees C .**

Polymer conc. ( wt% )	Log Polymer conc. (wt%)	Surface tension (mN/m) at day 1	S.T ( mN m ) after 96 days
0.00295	-2.530	69.63	70.94
0.0098	-2.009	68.60	66.34
0.0391	-1.408	66.69	58.55
0.0782	-1.107	59.94	53.89
0.1563	-0.806	55.55	47.72
0.3125	-0.505	52.45	43.00
0.625	-0.204	52.56	42.75
1.25	0.097	50.52	42.05
2.5	0.398	51.10	41.95
5.0	0.699	47.92	41.79

**Table 5.9:** The Surface tension-Time Data for Copolymer of  
 Maleic anhydride/1-dodecene, measured for  
 Polymer concentration of 5.0 wt% at 30 degree C .

Time (Day)	Sqrt time (Day) <sup>1/2</sup>	Surface tension (mN/m)
0.0	0.0	44.25
3.0	1.731	45.19
4.0	2.0	44.74
5.0	2.236	44.16

**Table 5.10: The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-dodecene, measured for  
Polymer concentration of 2.50 wt% at 30 degrees C .**

Time (Day)	Sqrt time (Day) <sup>1/2</sup>	Surface tension (mN/m)
0.0	0.0	45.00
0.73	0.854	46.61
1.0	1.00	44.69
1.7	1.304	41.52
2.0	1.414	42.78
4.7	2.168	41.07
5.0	2.236	41.82
5.7	2.387	39.52
6.1	2.470	37.66
7.8	2.793	36.17
8.8	2.966	34.90

Table 5.11: The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-dodecenc, measured for  
Polymer concentration of 1.25 wt% at 30 degrees C .

Time (Day)	Sqrt time (Day) <sup>1/2</sup>	Surface tension (mN/m)
0.0	0.0	47.21
2.80	1.673	44.23
3.8	1.949	44.84
4.6	2.145	43.91
6.0	2.449	44.33
6.8	2.608	44.35
10.0	3.162	43.46



Table 5.12: The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-dodecene, measured for  
Polymer concentration of 0.625 wt% at 30 degrees C .

Time (Day)	Sqrt time (Day) <sup><math>\frac{1}{2}</math></sup>	Surface tension (mN/m)
0.0	0.0	48.00
2.80	1.673	46.93
3.8	1.949	44.13
4.6	2.145	44.97
6.0	2.449	44.49
6.9	2.627	45.57
10.0	3.162	43.79

Table 5.13: The Surface tension-Time Data for Copolymer of  
 Maleic anhydride/1-dodecene, measured for  
 Polymer concentration of 0.0098 wt% at 30 degrees C .

Time (Day)	Sqrt time (Day) <sup>1/2</sup>	Surface tension (mN/m)
0.0	0.0	67.24
2.92	1.709	69.21
4.04	2.010	69.55
4.93	2.220	69.78
5.84	2.417	69.11
7.03	2.651	69.17
9.91	3.148	69.09

**Table 5.14:** The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-hexadecene, measured for  
Polymer concentration of 5.0 wt% at 30 degrees C .

Time (Day)	Sqrt time (Day) <sup>1/2</sup>	Surface tension (mN/m)
0.0	0.0	47.92
0.25	0.5	45.84
0.98	0.99	42.64
1.31	1.144	43.44
3.94	1.985	32.45
4.32	2.078	33.10
4.95	2.225	37.47
5.39	2.322	28.08
7.11	2.666	27.93
8.03	2.834	24.93

**Table 5.15: The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-hexadecene, measured for  
Polymer concentration of 2.5 wt% at 30 degrees C .**

Time (Day)	Sqrt time (Day) <sup>½</sup>	Surface tension (mN/m)
0.0	0.0	51.10
2.77	1.664	44.99
3.77	1.942	45.92
4.61	2.147	45.88
5.99	2.447	44.34
6.86	2.619	45.85
10.0	3.162	42.96

**Table 5.16: The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-hexadecene, measured for  
Polymer concentration of 0.3125 wt% at 30 degrees C .**

Time (Day)	Sqrt time (Day) <sup>1/2</sup>	Surface tension (mN/m)
0.0	0.0	52.45
2.76	1.661	44.54
3.76	1.939	47.36
4.604	2.146	48.96
5.98	2.445	47.23
6.85	2.617	48.74
9.99	3.161	46.99

**Table 5.17: The Surface tension-Time Data for Copolymer of  
Maleic anhydride/1-hexadecene, measured for  
Polymer concentration of 0.0098 wt% at 30 degrees C .**

Time (Day)	Sqrt time (Day) <sup>½</sup>	Surface tension (mN/m)
0.0	0.0	68.60
2.90	1.703	69.55
4.04	2.010	69.28
4.92	2.218	68.63
5.79	2.406	69.44
7.04	2.653	69.25
9.92	3.150	65.70

Table 5.18: The Surface tension-Time Data for Copolymer of  
 Malcic anhydride/1-hexadecene, measured for  
 Polymer concentration of 0.00295 wt% at 30 degrees C .

Time (Day)	Sqrt time (Day) <sup>½</sup>	Surface tension (mN/m)
0.0	0.0	69.63
2.90	1.703	69.53
4.04	2.010	69.68
4.92	2.218	70.01
5.79	2.406	69.95
7.04	2.653	69.72
9.92	3.150	69.84

Table 5.19: The Interfacial tension(aqueous solution/decane)-  
 Polymer concentration-NaCl concentration Data  
 for Copolymer of Maleic anhydride-1-dodecene,  
 measured at 40 degrees C .

NaCl conc (wt%)	IFT(mN/m) at 5 wt%polymer conc.	IFT(mN/m) at 2.5wt% polymer conc.
0.0	8.68	13.77
0.50	7.563	11.04
1.0	1.050	1.750



**Table 5.20:** The Interfacial tension(aqueous solution/decane)-  
Polymer concentration-NaCl concentration Data  
for Copolymer of Maleic anhydride/1-hexadecene,  
measured at 40 degrees C .

NaCl Conc (wt%)	IFT(mN/m) at 5 wt%polymer conc.	IFT(mN/m) at 2.5wt% polymer conc.
0.0	11.66	14.26
0.50	10.73	14.19
1.0	1.76	5.34

**Table 6.2:** The Viscosity-shear rate Data for Original  
Polyvinylalcohol (PVA) of Molecular weight 72,000 and for  
Polymer concentrations of 2.0 and 5.0 wt%, measured at 30 C.

Speed RPM)	Shear rate (1/sec)	Viscosity(cps) at 2.0 wt% conc	Viscosity(cps) at 5.0 wt% conc
60.0	79.2	4.5	39.2
30.0	39.6	4.7	39.7
12.0	15.8	5.0	40.1
6.0	7.9	6.0	42.8
3.0	4.0	***	48.4
1.5	2.0	***	65.1
0.6	0.8	***	96.2
0.3	0.4	***	145.0

**Table 6.3: The Viscosity-shear rate-Temperature Data**  
**for Urethanized PVA of Molecular weight of 72,000**  
**and for Polymer concentration of 1.8 wt% .**

Shear rate (1/sec)	Viscosity(cps) at 30 degree C	Viscosity(cps) at 50 degree C	Viscosity(cps) at 70 degree C
73.4	3.1	2.4	1.6
36.7	3.1	2.4	1.6
14.7	3.3	2.8	1.7
7.3	3.7	2.8	1.8
3.7	4.2	3.2	2.2

**Table 6.4: The Viscosity-Shear rate-Temperature Data**  
**for Urethanized PVA of Molecular weight of 72.000**  
**and for Polymer concentration of 5.0 wt% .**

Shear rate (1/sec)	Viscosity(cps) at 30 degree C	Viscosity(cps) at 60 degree C	Viscosity(cps) at 90 degree C
79.2	25.1	11.3	6.6
39.6	25.9	12.9	6.9
14.7	26.1	17.0	8.2
7.9	28.5	21.5	10.5
4.0	33.5	33.0	14.0
2.0	48.0	40.0	22.0
0.8	68.5	56.8	55.0
0.4	120	99.7	75.0

**Table 6.5: The Viscosity-Shear rate Data for**  
**Modified Polyvinylalcohol (PVA) with the hydrophobic**  
**combination of 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10,**  
**Molecular weight of 72,000 and for Polymer concs.**  
**of 4.0 and 5.0 wt%, measured at 30 degree C.**

Speed RPM)	Shear rate (1/sec)	Viscosity(cps) for 4.0 wt% conc	Viscosity(cps) for 5.0 wt% conc
60.0	79.2	25.7	51.4
30.0	39.6	26.8	52.5
12.0	15.8	28.5	65.3
6.0	7.3	35.9	80.95
3.0	3.7	45.0	100.6
1.5	1.8	55.6	139.9
0.6	0.7	83.0	175.41
0.3	0.4	155.0	300.0

**Table 6.6:** The Viscosity-Shear rate Data for  
 Modified Polyvinylalcohol (PVA) with the hydrophobic  
 combination of 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10,  
 Molecular weight of 72,000 and for Polymer concs.  
 of 0.5, 1.0, 2.0 and 3.0 wt%, measured at 30 degree C.

Speed (RPM)	Shear rate (1/sec)	Vis.(cps) at 0.5wt%	Vis.(cps) at 1.0wt%	Vis.(cps) at 2.0wt%	Vis.(cps) at 3.0wt%
60.0	73.4	1.30	2.10	6.40	13.2
30.0	36.7	1.36	2.20	6.50	13.2
12.0	14.7	1.55	2.40	6.52	13.2
6.0	7.3	1.75	2.60	6.54	13.5
3.0	3.7	****	****	****	14.8
1.5	1.8	****	****	****	16.8
0.6	0.8	****	****	****	****
0.3	0.4	****	****	****	****

**Table 6.7: The Viscosity-Shear rate Data for**  
**Modified Polyvinylalcohol (PVA) with the hydrophobic**  
**combination of 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10.**  
**Molecular weight of 100,000 and for Polymer concs.**  
**of 3.0, 4.0 and 5.0 wt%, measured at 30 degrees C.**

Speed RPM)	Shear rate (1/sec)	Vis.(cps) at 3.0 wt%	Vis.(cps) at 4.0 wt%	Vis.(cps) at 5.0 wt%
60.0	79.2	14.66	18.3	20.0
30.0	39.6	19.51	37.0	50.0
12.0	15.8	30.0	67.2	100.0
6.0	7.9	61.0	101.5	200.0
3.0	4.0	131.0	181.0	296
1.5	2.0	279.9	329.9	850.9
0.6	0.8	799.8	929.0	2424
0.3	0.4	1500.0	2100	3049

**Table 6.8: The Viscosity-Shear rate Data for**  
**Modified Polyvinylalcohol (PVA) the with hydrophobic**  
**combination of 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10.**  
**Molecular weight of 100,000 and for Polymer concs.**  
**of 1.0 and 2.0 wt%, measured at 30 degrees C.**

Speed RPM)	Shear rate (1/sec)	Viscosity(cps) at 1.0 wt% conc	Viscosity(cps) at 2.0 wt% conc
60.0	73.4	1.6	13.0
30.0	36.7	1.7	17.3
12.0	14.7	2.2	29.1
6.0	7.3	***	60.5
3.0	3.7	***	105.4
1.5	1.8	***	221.2
0.6	0.7	***	726.8
0.3	0.4	***	1342.2



**Table 6.9: The Viscosity-Shear rate-Temperature**  
**Data for Modified Polyvinylalcohol (PVA)**  
**with the hydrophobic combination of**  
**0.5mol%C22, 0.5mol%C18 & 1.0mol%C10,**  
**Molecular weight of 100,000 and for Polymer concs.**  
**of 2.0 wt%.**

Shear rate (1/sec)	Vis.(cps) at 30° C	Vis.(cps) at 40° C	Vis.(cps) at 50° C	Vis.(cps) at 60° C	Vis.(cps) at 70° C
73.4	13.0	8.50	6.60	5.18	4.9
36.7	17.3	12.9	10.4	8.16	7.0
14.7	29.1	20.7	20.4	16.0	10.5
7.3	60.5	51.9	39.7	31.14	20.5
3.7	105.4	103.0	79.8	62.6	30.6
1.8	221.2	204.0	158.0	123.92	74.1
0.7	726.8	549.0	446.0	349.8	190
0.4	1342.2	915.0	743.3	582.98	341

**Table 6.10: The Viscosity-Shear rate-Temperature**  
**Data for Modified Polyvinylalcohol (PVA)**  
**with the hydrophobic combination of**  
**0.5mol%C22, 0.5mol%C18 & 1.0mol%C10,**  
**Molecular weight of 100,000 and for Polymer concs.**  
**of 5.0 wt%.**

Shear rate (1/sec)	Vis.(cps) at 30 °C	Vis.(cps) at 40 °C	Vis.(cps) at 50 °C	Vis.(cps) at 60 °C	Vis.(cps) at 70 °C
79.2	20.0	19.2	13.95	10.16	7.4
39.6	50.0	38.4	27.90	20.27	12.8
15.8	100.0	96.0	69.76	50.69	24.5
7.9	200.0	192.0	139.5	101.36	50.2
4.0	296.0	256.0	182.0	132.23	93.22
2.0	850.9	347.6	239.0	173.65	122.43
0.8	2424.0	706.0	501.0	364.0	300
0.4	3049.0	1530	1110.0	806.5	461

**Table 6.11:** The Viscosity-NaCl Concentration Data  
 for Modified PVA with the hydrophobic combination of  
 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10, Molecular weight  
 of 72,000 and for Polymer concentration of 0.5 wt%,  
 measured, at 30 C and at Shear rate of 73.4 and  
 36.7 (1/sec).

NaCl conc (wt%)	Viscosity at S.R 73.4 $s^{-1}$	Viscosity at S.R 36.7 $s^{-1}$
0.0	1.30	1.36
0.1	1.32	1.40
1.0	1.35	1.42
2.0	1.29	1.35
5.0	1.37	1.47
7.0	1.38	1.48

Table 6.12: The Viscosity-Time(Ageing) Data for  
 Modified Polyvinylalcohol (PVA) with the hydrophobic  
 combination of 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10.  
 Molecular weight of 72,000 and for Polymer concs.  
 of 1.0, 2.0, 3.0 and 4.0 wt%, measured at 30<sup>o</sup> C.

Time (Week)	Viscosity(cps) for 1wt% conc	Viscosity(cps) for 2wt% conc	Viscosity(cps) for 3wt% conc	Viscosity(cps) 4wt %
0	2.60	6.80	13.8	25.7
1	2.51	5.55	12.2	23.4
2	2.40	4.30	10.6	21.0
3	2.33	4.30	10.23	19.8
4	2.27	4.30	9.87	18.6
5	2.2	4.30	9.50	17.4

Table 6.13: The Surface tension-Polymer concentration Data for Modified PVA with hydrophobic combinations of 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10 and Molecular weight of 100,000, measured at 30 degrees C .

Polymer conc. ( wt% )	Log Polymer conc. (wt%)	Surface tension (mN/m)
0.01	-2.0	54.67
0.10	-1.0	53.67
0.50	-0.301	49.19
1.00	0.0	44.77
2.00	0.301	42.81

**Table 6.14:** The Surface tension-Polymer concentration-Time Data  
for Modified PVA with the hydrophobic combination of  
0.5mol%C22, 0.5mol%C18 & 1.0mol%C10 and Molecular  
weight of 72,000, measured at 30 degrees C .

Poly. conc. ( wt% )	S.T1 (mN/m)	S.T2 (mN/m)	S.T3 (mN/m)	S.T4 (mN/m)	S.T5 (mN/m)	S.T6 (mN/m)	S.T7 (mN/m)
0.01	56.97	57.54	58.06	59.02	59.06	58.30	56.90
0.10	53.57	52.65	54.88	54.28	55.80	54.73	53.50
0.50	49.73	51.11	52.81	52.44	52.22	51.85	49.55
1.00	45.31	48.81	50.25	51.69	50.85	49.74	46.0
2.00	43.35	44.88	48.26	50.0	51.52	56.08	****

where

S.T1, S.T2, S.T3, S.T4, S.T5, S.T6 and S.T7 are the Surface tensions  
at day 1, day 2, day 4, day 6, day 8, day 9 and day 16

Table 6.15: The Surface tension-NaCl concentration Data for Modified PVA with the hydrophobic combination of 0.5mol%C22, 0.5mol%C18 & 1.0mol%c10, Molecular weight of 72,000, and for polymer concentration of 0.5 wt%, Measured 30 degree C .

NaCl conc. ( wt% )	Surface tension (mN/m)
0.1	49.83
1.0	48.61
2.0	47.34
4.0	45.26
7.0	43.02

Table 6.16: The Surface tension-Polymer concentration Data for  
Urethanized PVA of molecular weight of 72,000,  
measured at 30 degree C .

Polymer conc. ( wt% )	Log Polymer conc. (wt%)	Surface tension (mN/m)
0.01	-2.0	63.10
0.10	-1.0	60.37
0.50	-0.301	54.05
1.50	0.176	50.30
1.80	0.255	49.00
5.00	0.699	43.89



Table 6.17: The Surface tension-Polymer concentration Data for  
Original PVA of molecular weight of 72,000,  
measured at 30 degree C .

Polymer conc. ( wt% )	Log Polymer conc. (wt%)	Surface tension (mN/m)
0.01	-2.0	70.0
0.05	-1.301	66.0
0.1	-1.0	65.50
0.2	-0.699	64.00
0.3	-0.523	63.50
0.4	-0.399	62.00
0.5	-0.301	61.75
1.0	0.0	56.75
2.0	0.301	51.70

**Table 6.18:** The Interfacial tension(aqueous solution/decane)-  
 Polymer concentration-NaCl concentration-  
 Polymer solution Density Data for  
 Modified PVA with the hydrophobic combination of  
 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10, and Molecular  
 weight of 72,000, measured at 25 degrees C .

NaCl Conc (wt%)	IFT(mN/m) at 0.5wt% conc.	IFT(mN/m) at 2.0wt% conc	Density g/cm,0.5wt%	Density g/cm,2.0wt%
0.0	14.21	10.81	1.009	1.017
1.0	13.19	9.72	1.015	1.023
3.0	8.38	4.81	1.028	1.036
5.0	4.25	1.11	1.042	1.048
7.0	1.49	0.47	1.055	1.061

Table 6.19: The Interfacial tension(aqueous solution/decane)-  
 Polymer concentration-NaCl concentration-  
 Polymer solution Density Data for  
 Modified PVA with the hydrophobic combination of  
 0.5mol%C22, 0.5mol%C18 & 1.0mol%C10, and Molecular  
 weight of 100,000, measured at 25 degrees C .

NaCl Conc (wt%)	IFT(mN/m) at 0.5wt% conc.	IFT(mN/m) at 2.0wt% conc	Density g/cm,0.5wt%	Density g/cm,2.0wt%	Dcn. 5.0%
0.0	11.10	10.16	1.0084	1.0172	1.0330
1.0	10.11	9.26	1.0155	1.0235	1.0395
3.0	5.25	4.35	1.0292	1.0362	1.0525
5.0	2.00	0.85	1.0428	1.0488	1.0655
7.0	1.08	0.15	1.0565	1.0615	1.0785

Table 6.20: The Interfacial tension(aqueous solution/deccane)-  
NaCl concentration-Polymer solution Density  
Data for Urethanized PVA of molecular weight  
of 72,000, measured at 25 degree C .

NaCl Conc (wt%)	IFT(mN/m) at 2.0 wt% conc	Density g/cm at 2.0 wt%conc.
0.0	12.95	1.014
1.0	11.99	1.020
3.0	10.05	1.033
5.0	9.69	1.0460
7.0	8.54	1.0590

where

Density of Decane = 0.74 g/cubic cm

Table 6.21: The Viscosity-Shear rate-Polymer conc.

Data for Modified PVA with the Hydrophobic Combination  
of 2.0mol%C18 &1.0molC10, and Molecular weight of  
72,000, measured at 30 degree C

Shear rate (1/sec)	Vis. at 1wt conc	Vis. at 2wt% conc	Vis. at 3wt% conc	Vis. at 3wt% conc 5wt% NaCl
79.2	2.01	9.30	****	****
39.6	2.01	9.60	****	****
15.8	2.81	10.0	****	****
7.9	4.00	11.5	369.0	382
4.0	5.00	12.0	384.0	421
2.0	10.0	14.0	431.0	469
0.8	20.0	30.1	509.0	601
0.4	30.01	70.1	651.0	862

**Table 6.22: The Viscosity-NaCl concentration Data**  
**for Modified PVA with the hydrophobic combination**  
**of 2.0mol%C18 &1.0mol%C10, and Molecular weight 72,000,**  
**measured at 30 degree C, for polymer conc. of 3.0 wt%**

NaCl conc. ( wt% )	Viscosity ( cps )
0.0	369
1.0	386
3.0	219
5.0	382
7.0	401

**Table 6.23: The Surface tension-Polymer concentration Data for Modified PVA with the hydrophobic combination of 2.0mol%C18 & 1.0mol%C10, Molecular weight of 72,000, measured at 30 degrees C .**

Polymer conc. ( wt% )	Surface tension (mN/m) at 0wt% NaCl	Surface tension (mN/m) at 5.0wt% NaCl
0.01	60.12	58.50
0.1	58.88	57.34
0.5	56.25	54.99
1.0	54.58	52.94
2.0	50.26	49.01
3.0	42.41	41.15
4.0	37.23	36.00
5.0	28.56	27.30

## APPENDIX B



**MODIFICATION OF URETHANIZED POLYVINYLALCOHOL (PVA)  
WITH THE THREE ACID CHLORIDES.**

Acid chlorides Molecular Weight

$$(A) \text{ (CH}_3\text{(CH}_2\text{)}_8\text{COCl) = 190.5g}$$

$$(B) \text{ (CH}_3\text{(CH}_2\text{)}_{16}\text{COCl) = 302.5g}$$

$$(C) \text{ (CH}_3\text{(CH}_2\text{)}_{20}\text{COCl) = 358.5g}$$

Amount of urethanized PVA with molecular weight of 72,000 = 4.0 g

$$\text{No. of mole of urethanized PVA repeat unit} = \frac{4.0\text{g}}{48.4\text{g}}$$

10% degree of urethanization (DU) is assumed in this calculation for the urethanized PVA; thus the molecular weight of the urethanized PVA repeat unit is 48.4 g.

**Example#1**

For Hydrophobic combinations of 0.5 mol%  $\text{(CH}_3\text{(CH}_2\text{)}_{20}\text{COCl)}$ , 0.5 mol%  $\text{(CH}_3\text{(CH}_2\text{)}_{16}\text{COCl)}$  and 1.0 mol%  $\text{(CH}_3\text{(CH}_2\text{)}_8\text{COCl)}$ .

$$\text{I. Amount of 0.5 mol\% (CH}_3\text{(CH}_2\text{)}_{20}\text{COCl) = } \frac{0.5}{100} * \frac{4.0}{48.4} * 358.5 = 0.148\text{g}$$

$$\text{II. Amount of 0.5 mol\% (CH}_3\text{(CH}_2\text{)}_{16}\text{COCl) = } \frac{0.5}{100} * \frac{4.0}{48.4} * 302.5 = 0.125\text{g}$$

$$\text{III. Amount of 1.0 mol\% (CH}_3\text{(CH}_2\text{)}_8\text{COCl) = } \frac{1.0}{100} * \frac{4.0}{48.4} * 190.5 = 0.157\text{g}$$

**Example#2**

For Hydrophobic combinations of 2.0 mol%  $(\text{CH}_3(\text{CH}_2)_{16}\text{COCl})$  and 1.0 mol%  $(\text{CH}_3(\text{CH}_2)_8\text{COCl})$ .

Amount of urethanized PVA with molecular weight of 72,000 = 10 g

$$\text{No. of mole of urethanized PVA} = \frac{10}{48.4}$$

$$\text{I. Amount of 2.0 mol\% } (\text{CH}_3(\text{CH}_2)_{16}\text{COCl}) = \frac{2.0}{100} * \frac{10.0}{48.4} * 302.5 = 1.25\text{g}$$

$$\text{II. Amount of 1.0 mol\% } (\text{CH}_3(\text{CH}_2)_8\text{COCl}) = \frac{1.0}{100} * \frac{10.0}{48.4} * 190.5 = 0.394\text{g}$$

**HYDROLYSIS OF COPOLYMERS OF MALEIC ANHYDRIDE/1-ALKENE.**

Molecular Weight of Maleic anhydride = 98.06 g

Molecular Weight of 1-dodecene = 168.32 g

Molecular Weight of 1-hexadecene = 224.43 g

For the hydrolysis of the copolymers with NaOH,

1 mole of Maleic anhydride is required for 2 moles of NaOH.

**Example#1**

For 2.66 wt% polymer concentration of copolymer of maleic anhydride/1-dodecene

$$\text{No. of mole of 0.2M NaOH in 50 ml solution} = \frac{50}{1000} * 0.2 \text{ M} = 0.01 \text{ mole}$$

$$\text{No. of mole of maleic anhydride} = \frac{0.01}{2} \text{ mole}$$

$$\text{Thus, the amount of polymer required} = \frac{0.01}{2} * 266.38 = 1.332\text{g}$$

### Example#2

For 3.2 wt% polymer concentration of copolymer of maleic anhydride/1-hexadecene

$$\text{No. of mole of 0.2M NaOH in 50 ml solution} = \frac{50}{1000} * 0.2 \text{ M} = 0.01 \text{ mole}$$

$$\text{No. of mole of maleic anhydride} = \frac{0.01}{2} \text{ mole}$$

$$\text{Thus, the amount of polymer required} = \frac{0.01}{2} * 322.49 = 1.6125\text{g}$$